

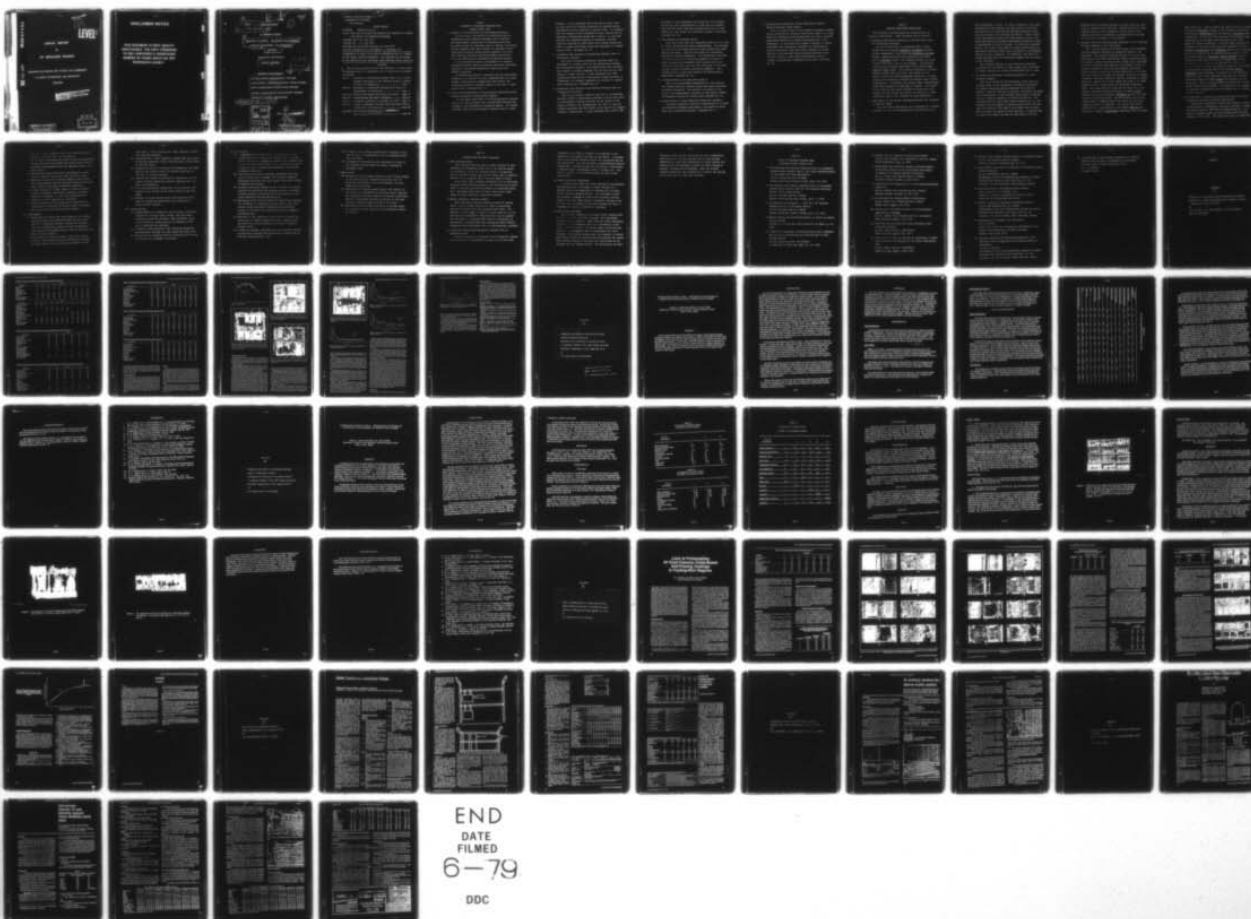
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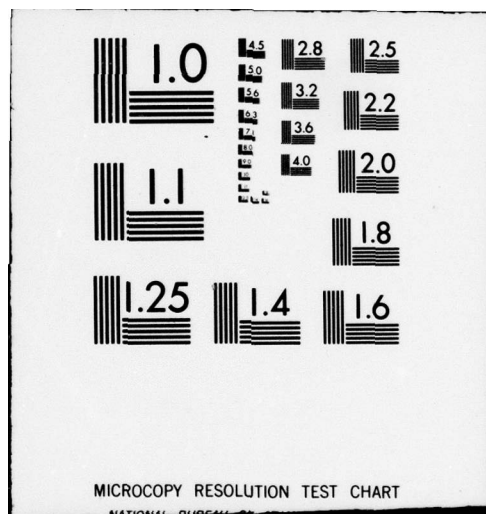
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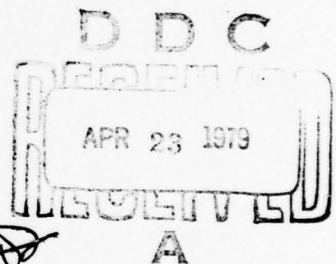
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ORGANISMS OF DISEASE AND FOULING AND CORROSION
IN MARINE ENVIRONMENT AND PROTECTIVE
MEASURES.

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ABSTRACT

The previous detailed report was submitted in August 1976.
The present report is subdivided into 6 parts and an Appendix
as follows:

PART I : Abstracts of Published Research Work in the Period between Submission of the Previous Detailed Report and Now. (8 Abstracts)	Page 2
PART II : Abstracts of Completed Research Work Ready for Publication. (5 Articles)	Page 6
PART III: Current and Future Activities (28 Items)	Page 11
PART IV : Installations and Major Equipment	Page 16
PART V : Financial Situation on December 31, 1978	Page 19
PART VI : Titles of Relevant Research Work Published before August 1976. (19 Articles)	Page 20
Appendix: Photocopies and Reprints of Abstracts of Part I publications	Page 24

PART I

ABSTRACTS OF PUBLISHED RESEARCH WORK

(August 1976 - Now)

1. Advances on Anticorrosive and Antifouling Coatings.

In this paper, the merits of introducing lamellar aluminium in anticorrosive coatings, and a swellable non-hydrolyzable plasticizer in antifouling coatings are demonstrated by long-term tests in natural environment. It was concluded that raft testing in a natural environment which combines rather severe climatic conditions with nontoxic pollution provides valuable information as to the efficiency of underwater protective systems.

In anticorrosive paints, incorporation of lamellar aluminium provides better protection than when inhibiting pigments of the anodic passivation types were used without aluminium.

In antifouling paints, a swellable but nonhydrolyzable plasticizer is superior to both nonhydrolyzable and hydrolyzable counterparts in regulating toxin release and allowing retention of surface copper in the form of basic copper salts. (Document No. 1).

2. Limit of Protectability of Vinyl-Cuprous Oxide-Based Antifouling Coatings in Fouling-Rich Regions.

In this paper three sets of antifouling paints varying only in the Cu_2O contents were prepared and submerged for testing in the fouling-rich Alexandria Harbor. The series included paints with the maximum tolerable cuprous oxide

content. It was concluded that there was an upper limit for the period for fouling prevention by coatings mainly depending for their toxicity on cuprous oxide. It appeared that the maximum period attainable by such compositions in temperate, fouling-rich waters is 13 months. It was advised that for extended periods of protection, research should be directed to areas where other binder systems are used, or higher efficiency toxics may supplement or replace cuprous oxide. (Document No. 2).

3. Preparation and Testing of Antifouling Coatings Based on Tributyltin Fluoride.

This paper presents tributyltin fluoride (TBTF) as alternative to cuprous oxide in the antifouling coatings for fouling-rich regions. The results were very promising with respect to animal organisms but not very much so with respect to plant fouling. It was concluded that TBTF formulations function by a slow-release mechanism which is independent of a soluble ingredient in contrast to cuprous oxide formulations. (Document No. 3).

4. Preparation and Testing of Antifouling Coatings Based on Triphenyltin Fluoride.

This is an extensive study on the role of triphenyltin fluoride (TPTF) on antifouling coatings in which three sets of environmental testing took care of the effect of the amount of TPTF in the formulations, the role of rosin as soluble ingredient and the effect of the type of the pigment extender, respectively. It was concluded that TPTF at 20%

by weight in the formulation was sufficient for longterm protection, that incorporation of rosin was of disadvantage and that china clay and lithopone were the best and barytes was the poorest for efficient longterm protection. (Document No. 4).

5. Some Studies on Aluminium Paints

This paper deals with the preparation and use of coating for steel structures for marine applications. The coatings are meant for preventing corrosion under antifouling coatings in sea water. They are also meant for preventing corrosion in marine atmosphere. The conclusions were that aluminium paints with chlorinated rubber or a blend of vinyl copolymer and coumarone-indene resin showed good corrosion resistance, and that the efficiency of the coating was improved by adding inhibitive pigments. Also, incorporation of china clay improved the anticorrosion efficiency. (Document No. 5).

6. A testing Station for Above-Water Paints.

This is an illustrated description of a new station for testing different metals, alloys and coated materials in marine atmosphere. The station is situated on the roof of the Oceanographic Institute on the eastern harbor of Alexandria facing the testing raft (Document No. 6).

7. Classification of Some Commercial Inhibitive Pigments.

The paper describes a method of classification of seven new inhibitive pigments according to the manner by which they yield inhibitive material. (Document No. 7).

8. Anti-Corrosion Behaviour of Some Laboratory Prepared Barium Metaborate Based Paints.

This is a short review of an extensive program employing barium metaborate as corrosion inhibiting pigment in a large number of formulations and testing them for their corrosion protecting properties in marine environment and in the laboratory. It was found that surface treatment of barium metaborate with silica was important for achieving the desired properties, that some binder systems are better than the others and that barium metaborate-based paints are more suited to above water constructions than to surfaces continuously submerged in sea water. (Document No. 8).

PART II

RESEARCH WORK UNDER PUBLICATION

The following research papers are completed and are ready for publication. Their abstracts are as follows:

1. Settlement and Larval Behaviour of the Tube Worm *Spiro-rbis corrugatus* Montague.

The work carried out in Alexandria easter harbor showed that the serpulid Spōrorbis corrugatus Montague settled abundantly on the green alga Caulerpa prolifera Forssk. Worms were found more numerous on the basal part of Caulerpa blades. The distance between the newly settled worms was 1.9 mm on the average. In laboratory settling larvae showed indifferent choice between Caulerpa and Ulva blades. The greatest liberation of larvae occurred between April and June. The larvae of this species carried two large attachment glands and it passed through rapid swimming, rotation and crawling stages before metamorphosis. Laboratory tests proved that metamorphizing larvae were negative to light and to gravity. The length of the larval period never exceeded 12 hours after liberation but this period was shorter in darkness, at high temperatures and in the presence of rough substrates.

2. High Copper in the Waters, Suspended Material and Sediments in the Suez Canal.

This work was stimulated by the increasing ship traffic through this important waterway since its reopening for

world navigation in 1975. In view of absence of any copper contamination from without, the only source of pollution was believed to be antifouling coatings extensively used until the present time for ship protection. Atomic absorption measurements proved very high copper in water, suspended material and sediments indicating accumulation which is unsurpassed by tide or current. In water and suspended matter, the results show peaks of copper concentrations at particular locations which could be ascribed to hydrological factors and ship schedules. In sediments, the amount of copper depended upon the extracting reagents and the nature of the substrate.

The potential dangers of this situation stimulated investigations of effects of other heavy metal pollutants on chronic toxicity in fouling invertebrates and in fish.

3. The Inhibition Mechanism of Barium Metaborate as Anti-corrosive Pigment.

This is an extensive electrochemical study aiming at throwing light on the mechanism of corrosion prevention by coatings employing barium metaborate as inhibitive pigment. From the electrode potential, resistance and weight loss measurements, it was concluded that barium metaborate acts as an anodic inhibitor of limited solubility. Its solution under the paint film has an alkaline pH 9.3. The hydroxyl ions are capable of giving protection at this pH, since the effect of the borate is to buffer the solution and so prevent the anodic pH from falling. It appears that as long as the anodic pH does not drop below 9 ferrous

hydroxide can be rapidly oxidized to ferric oxide and thus leads to inhibition of corrosion. Modification with sodium silicate which is later changed to silica improves the pigment properties by reducing its solubility and raising the electrode resistance of the coating. ;

4. Seasonal Variation and Settlement Behaviour of the Principal Fouling Organisms in the Suez Canal.

This is an extension of the wide study of the principal fouling organisms performed in Alexandria harbor a few years ago. The present study was carried out on two successive years 1977-1978 with monthly sample collecting trips. The survey included settlement rate, growth rate, influence of depth on quantity and quality of settlement, effect of surface orientation and color and seasonal succession. Twelve sampling sites were selected along the 165 km waterway: Port-Said, Ras El-Esh, El-Kantara, El-Teena, El-Ballah, El-Ferdan, Ismailia, Defresoir, Kabrit, El-Shaloufa, Genefa and Suez. Fouling in the Suez Canal was found to be dense except in Suez. Growth rates are generally remarkably high. Some organisms were found for the first time, for example, molluscan bivalves belonging to genus Amonia. Invasion by isopods especially Sphaezoma sp which are wood borers was also discovered. The most severe fouling was always found in Ismailia waters for which the following summary is given: In February - the lowest temperature month (17°C) - large number of tube worms (Hydroids and Spirorbis), Bryozoa (Bineritina), Amphiboda tubes and green

algae prevailed. During Spring, the species number increased. In addition Ascidians (Ciona), three species of barnacles, particularly B-Amphitrite and the bryozoan B-turbinata were encountered. In May the tube worms were the dominant organisms and the whole panels were covered by more than 4 species of these polychaetes. The tube worms continued to dominate the fouling in June and were accompanied by the barnacles B-Amphitrite and B-eburneus which were mostly dead due to the invasion by the abovementioned isopods. There were many ascidians (Diplosoma, Styela partita) and the fouling of each panel (15 x 15 cm) weighed about 250 g. In July the net weight of the fouling of a single test panel reached 200 g and the barnacles (about 400 specimens on each panel) comprised 70% of the fouling; Balanus amphitrite being dominant. In addition to the barnacles there were tube worms, Amphipoda tubes and the molluscan bivalves belonging to genus Amonia was observed for the first time. Data of similar nature are collected at each of the twelve sites selected. The results are too exhaustive and the correlations are too elaborate to be covered in this abstract.

5. The Synthesis of Organotin Polymers and Their Testing as Antifouling Coatings in Natural Environment.

Tributyltin methacrylate (TBTMA) was prepared through esterification of methacrylic acid with tributyltin oxide. The monomer had M.P. 18°C after recrystallization. Tributyltin acrylate (TBTAA) was also prepared and recrystallized to a M.P. 75°C. The reactivity ratio of TBTMA and

methyl methacrylate (MMA) was determined by the Fineman and Ross Method. The reactivity ratio of TBTMA and butyl methacrylate (BMA) was also determined. The copolymerization of TBTMA-MMA and TBTMA-BMA were found to show azeotropic copolymerization at certain mole ratios. The azeotropic composition of each system was polymerized to a high conversion and was found to give a homogeneous copolymer regardless of conversion (up to 90% conversion) with a constant tin content.

From the monomer reactivity ratios determined for the systems of TBTMA-MMA and TBTMA-BMA, the monomer reactivity ratio of MMA with BMA was calculated. Thus, the monomer reactivity ratios for the terpolymer, r_{12} , r_{21} , r_{13} , r_{31} , r_{23} and r_{32} were found.

From these six reactivity ratios, the azeotropic terpolymerization composition was calculated. This azeotropic terpolymerization composition was verified experimentally and was found to give a homogeneous terpolymer with a constant tin content regardless of conversion.

Terpolymers with different tin contents were prepared from interaction of BMA-TBTMA-MMA in different molar ratios including the azeotropic composition - to give tin contents of 15.9, 19.1 and 24.0%, respectively. These polymers were found to be soluble in many organic solvents. Their solutions were found to give strong adherent films on P.V.C. sheets and were not affected by salt water for long immersion times.

Pigmented (with TiO_2) and non-pigmented films of the above terpolymers on P.V.C. sheets were submerged in the marine testing station in Alexandria harbor on August 18, 1978. According to the last inspection report dated December 30, 1978 all panels are 100% free of macro-fouling.

PART III
CURRENT AND FUTURE ACTIVITIES

The current and future activities can be read out from a new "Proposal for a Research Project" submitted to the Ocean Science and Technology Division of the Office of Naval Research. The Proposal is in fact an extension to the present contract with the Microbiology Division of the same Office. Its general objectives are to expand studies of coastal sea water and land adjacent to the sea for corrosion, and fouling and boring organisms, and to continue developing, testing, and using environmentally competent protective coatings for metals, concrete and wood surfaces used in or near sea environment and the best methods for surface preservation.

A summary of the current and future activities is as follows:

I. Fouling and Wood Borer Organisms:

1. Identification, for the rest of the second running year, the monthly settling of marine fouling organisms along the Suez Canal from Port-Said in the North to Suez in the South, including settlement rate, growth rate, influence of depth on quantity and quality of settlement, and the seasonal succession.
2. Concluding and up-to-dating the fouling picture from Alexandria to Port-Said East, and from Port-Said to Suez South.
3. To find relationships between reproduction and propagation of fouling organisms, and fecal pollution. (Some of the

Floating testing stations being near untreated-sewage disposal pipes will help these studies).

1-, 2- and 3- are useful not only for work on antifouling coatings but also for current and future plans of constructional developments along the Egyptian coast, e.g., power plants.

4. Identification and growth rate determination of wood borers at various sites (see item 26 in this list).
5. Laboratory rearing of the larval stages of wood borers until metamorphosis and the relative infection of different kinds of wood under different conditions.
6. Wet-lab cultures of larval stages of various fouling animals (Ascidians, tube worms, molluscs, hydroids, barnacles, bryozoans ... etc) for determining the duration of each stage and its mortality.
7. Specific studies on the mechanism of settlement vs. repellancy or mortality of fouling larvae of polymers and coatings of toxic and non-toxic natures.

II. Hydrography:

8. Completing the work on the high copper in the waters, suspended matter and sediments along the Suez Canal (165 km) by finding relations between the observed state of equilibrium in favor of toxin accumulation and various environmental factors such as currents, and tides, and ship traffic.
9. Determination of toxic elements, other than copper, emerging from anticorrosion and antifouling coatings or other sources in the waters and sediments of the

Suez Canal. These elements are: lead, cadmium, arsenic, tin, zinc and chromium.

10. Determination of toxic elements in whole body and tissue of fouling organisms, flesh, bone and guts of fish native in the Suez Canal.
11. Comparative study of the waters of Alexandria, Port-Said and Suez for organic matter of various kinds and its relation to fouling flourish.
12. Hydrological factors governing the infestation by wood borers including salinity, calcium, magnesium and sulphate determination.
13. The origin nature and composition of the peculiar salt deposit at the bottom of the Bitter lakes at the Suez Canal.
14. Analysis of black bottom deposits and adjacent water layer at commercial harbor and their influence on materials and coatings.

III. Anticorrosion:

15. Establishment of a durability and corrosion resistance program for testing metals, alloys, wood and other materials coated and uncoated, under different climatical conditions, mainly marine, to optimize on the use of materials and coatings.
16. Underwater physical-barrier and inhibitor-containing anticorrosion coatings for ship bottom and water line.
17. New methods of applying cathodic protection and the use of sacrificial replacable electrodes.

IV. Antifouling:

18. An **expanded** formulation-testing program for classical cuprous-oxide based antifouling coatings in five localities of different fouling intensities for establishing the highest protection limit of these formulations with respect to the prevailing hydrographical, fouling and pollution conditions.
19. Formulating antifouling coatings containing both Cu_2O (for its wide toxic coverage) and selected organotin compounds (for their low toxic impact) and their testing in natural environment.
20. Extended laboratory studies on the synthesis of surface coatings of copolymers and terpolymers with one monomer bearing organotin moiety and their application in properly formulated antifouling coatings.
21. Continuing search for new non-toxic antifouling coatings for extending the protection period from 30 days (the period already achieved in fouling-rich Alexandria harbor) to 6 months (the period specified in standard specifications).
22. Devising in vivo facility in a wet lab for testing the efficiency of combined Cu_2O -organotin, organotin, and non-toxic antifouling coatings in repelling specific fouling larvae.
23. A study of problems connected with the interface between anticorrosion coatings and antifouling coatings such as cohesion, compatibility, etc.

24. A study of the coatings systems most competent in the Red Sea area in collaboration with the Ghardaga Institute personnel.
25. A program of substitution and replacement of some of the imported raw materials for marine coatings by indigenous ones.

V. Wood Borers:

26. Continuing the biological studies on wood borers aiming at characterization, seasonal variations, etc. at different localities in the Mediterranean, the Suez Canal and the Red Sea.
27. Continuing the technological studies with respect to the extent of infestation of different woods, imported and indigenous, by wood borers in different localities, aiming at specifying infested localities on one hand the most resistant kinds of wood on the other.
28. Processing wood for high resistance to borers attack by imprigation with extracts or preservatives and/or by coatings.

PART IV

Installations and Major Equipment

1. Five Testing Rafts:

Five testing rafts are now in normal function at five different environmental sites; one in the western harbor of Alexandria, one in the eastern harbor of Alexandria, one in Port-Said harbor, one in the Timsah lake at Ismailia and one at the Southern end of the Suez Canal at Suez.

These rafts offer valuable information on the hydrology, fouling ecology and wood borers at the selected sites which serve to optimize protective measures for submerged material. Materials under test in these rafts cover a wide range of metals and wood, coated and uncoated.

2. Marine Atmosphere Exposure Stands:

Five atmosphere exposure stands-inclined 45° facing South - are in normal function at various interesting near-sea locations near the aforementioned rafts. The capacity of each stand is about 85 plates each 15 x 15 cm. The aim is to establish a "corrosion map" and to compare the resistance to corrosion and erosion of materials of construction, coatings and other substances under various climatical conditions which will be simultaneously recorded.

3. A Chemical-hydrological-Biological Research Unit in Alexandria Area:

A modern design of a laboratory unit serving the research team is now under construction on part of a 20 acre land

belonging to the NRC at a suburb of Alexandria in the South-east only about 2 km from the sea shore. A microbus will be at constant service between the laboratory and the sea facilities. The unit includes a hydrographical-chemical laboratory, a marine biology lab, an office, a store-room, a reading room, a photography room, a terrace, etc. The unit is expected to be completed near the end of this year (1979).

4. Atomic Absorption Instrument:

A Perkin-Elmer model 370 atomic absorption spectrometer was purchased and is already in normal function in a special room at the laboratory of Polymers and Coatings of the National Research Centre. The instrument serves the extensive program of heavy metal pollution particularly in the Suez Canal waters, determines leaching rates of copper and organotin antifouling coatings and assists defining the nature of underwater sediments.

5. Other Major Equipment:

All research groups are now almost fully equipped with the needs as given in items "Equipmen and "Consumable Supplies" of the project. Apart from the atomic absorption instrument, the hydrology group is in possession of all basic gear and chemicals for proper sample collection and analysis. A salinometer and an autoanalyzer are still lacking. The fouling ecology team, now expanded to include wood borers studies is equipped with microscopes and cameras. Their monthly visits to the sites are facilitated by the microbus and its regular driver. The antifouling and anti-

corrosion teams have not completed yet their preparation, application and testing equipment and yet has already established a world wide reputation for their created formulations and the impressive results of their testing in natural, fouling-rich environment. When the already ordered instruments and equipment are received the quality of the work will be even more exciting.

PART VI

TITLES OF RELEVANT RESEARCH WORK

(Published before August 1976)

1. The Physical and Chemical Characteristics of Alexandria Western Harbor Waters. Part I. The Unique Characteristics of the Harbor and Work Orientation.
By N.A. Ghanem and M.M. El-Awady
Marine Technology Society Journal, 9(5), 41, 1975.
2. The Physical and Chemical Characteristics of Alexandria Western Harbor Waters. Part II. The Physical Characteristics of the Harbor Waters.
By M.M. El-Awady and N.A. Ghanem
Marine Technology Society Journal, 9(6), 3, 1975.
3. The Physical and Chemical ... Part III. The Chemical Characteristics of the Harbor Waters.
By M.M. El-Awady and N.A. Ghanem
Marine Technology Society Journal, 9(6), 12, 1975.
4. Marine Fouling and Antifouling Paints (A review in Arabic)
By N.A. Ghanem
Journal of Military and Civil Industries of Egypt, 1, 42, 1964.
5. A Modified Preparation of Sodium Diethyl Dithio Carbamate and its Use in Determining the Leaching Rate of Anti-fouling Paints.
By N.A. Ghanem and M.M. Abd El-Malek
J. Chemistry of Arab Rep. Egypt, 9, 377, 1966

6. Composition and Leaching of Antifouling Paints.
By M.M. Abd El-Malek, M.A. Abou-Khalil and N.A. Ghanem
Paint Manufacture, 10, 32, 1970.
7. Compounding and Testing of Weather Resistant Rubber.
Antioxidant Effects on the Accelerated Light-Aging
of Rubbers of Different Network Structures.
By A.A. Yehia, W.D. Khalifa and N.A. Ghanem.
European Polymer Journal, 7, 549, 1971.
8. Crosslinking and Degradation of a Side-Chain-Unsaturated
Polyester.
By N.A. Ghanem, M.H. Nosseir and N.I. Hussein
European Polymer Journal, 7, 943, 1971.
9. A New Device for Testing Rubber Vulcanizates.
By A.A. Yehia, N.A. Ghanem and W.D. Khalifa
Rubber World, 164(1), 68, 1971.
10. Composition and Characteristics of Some Underwater
Anticorrosion Coatings.
By N.A. Ghanem, A.B. Moustafa and M.A. Abou-Khalil
Farbe und Lack, 77(10), 961, 1971.
11. Zinc Dust and Zinc Dust-Zinc Oxide Underwater Anti-
corrosion Coatings.
By N.A. Ghanem and M.A. Abou-Khalil
Farbe und Lack, 79(3), 201, 1973.
12. Compositional Factors Affecting the Efficiency of Under-
water Anticorrosion Coatings of the Anodic Passivation
Type.
By N.A. Ghanem and M.A. Abou-Khalil
Farbe und Lack, 79(11), 1041, 1973.

13. A Novel Marine Paints Testing Station in Alexandria Harbor
By M.M. Abd El-Malek and N.A. Ghanem
Journal of Paint Technology, 47, 75, 1975.
14. Some Factors Affecting the Efficiency of Underwater Anti-corrosion Paints.
By M.A. Abou-Khalil and N.A. Ghanem
Proceedings of the 4th International Congress on Marine Corrosion and Fouling, 14-18 June 1976, pp. 43.
C.R.E.O., 73, Rue de Sevres, 92100 Boulogne, France.
15. Fouling Ecology in Alexandria Eastern Harbor.
M.Sc. Thesis by A.H. Megally, 1972
Faculty of Science, Alexandria University, Thesis supervised by El-Maghraby and Ghanem.
16. Effect of Rosin on High-Toxin Antifouling Paints.
By M.M. Abd El-Malek and N.A. Ghanem
Proceedings of the 4th International Congress on Marine Corrosion and Fouling, 14-18 June 1976, pp. 33.
C.R.E.O., 73, Rue de Sevres, 92100 Boulogne, France.
17. Interaction of Coatings with Environment
By N.A. Ghanem
Paper read at the 2nd International Conference on the Science and Technology of Surface Coatings.
Athens, July 19-24, 1976.
18. Seasonal Variation and Settlement Behaviour of the Principal Fouling Organisms in the Eastern Harbor of Alexandria.
By A.F.A. Ghobashy
Proceedings of the 4th International Congress on Marine Corrosion and Fouling, 14-18 June 1976. pp. 213
C.R.E.O., 73, Rue de Sevres, 92100 Boulogne, France.

19. A Preliminary Microbiological Examination of Coastal
Waters North and East of Alexandria in Non-Sewage
Disposal Sites Between June-August 1976.

By A. El-Lakany

Internal Report.

Appendix

DOCUMENT

(1)

Advances in Antifouling and Anticorrosive Coatings.
Industrial and Engineering Chemistry, Product Research
& Development, 17, 44, 1978.

By

N.A. Ghanem, M.M. Abd El-Malek, M.A. Abou-Khalil
and M.M. El-Awady.

Advances in Anticorrosive and Antifouling Coatings

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The reasons why the waters of Alexandria's eastern harbor present an interesting natural spot for testing underwater protection coatings are given. In continuation of a program for establishing structural properties relationships in anticorrosive and antifouling paints, well formulated protective systems are proposed encompassing up-to-date international industrial trends of ingredients and techniques. In this paper, the merits of introducing lamellar aluminum in anticorrosive coatings, and a swellable nonhydrolyzable plasticizer in antifouling coatings of otherwise unified composition are demonstrated by long-term tests in natural environment. Correlation is given between the laboratory determined leached toxicity from the widely used cuprous oxide antifouling coatings and their effectiveness in preventing fouling in the natural environment. Laboratory as well as in-nature tests exhibit distinctive mechanistic differences among formulations differing from each other only by the type of a minor constituent: the plasticizer.

Introduction

The waters of Alexandria's eastern harbor provide a very interesting marine locality for testing underwater coatings systems (Abd El-Malek and Ghanem, 1975). The water is almost free of oil and toxic pollutants, rich in fouling organisms,

is always above 21 °C (except between December and March), and is constant in salinity at about 3.8‰ throughout the year. The pH value ranges from 8 to 8.3, which is similar to that of natural sea water in the open sea, and the dissolved oxygen content is very close to 3.5 mL/L except in the less warm

months when values near 6 mL/L are reached (Megally, 1970).

Trials to establish underwater coatings systems which protect steel from corrosion and fouling for reasonable periods of time were carried out continuously during the last years in a specially built station floating in the vicinity of the Institute of Oceanography and Fisheries where the final preparations for the tests were performed.

The trials were guided by the results of a systematic program of analysis and testing anticorrosive and antifouling coatings of various natures. The work included quantitative compositional characteristics of the respective coatings (Ghanem et al., 1971; Abou-Khalil et al., 1970) and the impact of the composition on the performance of the coating in the laboratory and in nature. For anticorrosive coatings, the laboratory tests included water uptake, electrode potential of coated steel, electrical resistance of the film, and pH of pigment extract after long periods of immersion (Ghanem et al., 1971, 1973a,b). For antifouling coatings of the copper type, the laboratory tests comprised accelerated glycine and acid-alkali tests as well as normal leaching rate tests (Ghanem and Abd El-Malek, 1966; Hippi et al., 1962; Marson, 1964; U.S. Naval Institute, 1952). Laboratory tests on organometallic-containing antifouling coatings which are gaining commercial importance are being performed using a newly developed neutron activation analysis technique (Ghanem et al., unpublished data).

Incidentally, successful raft-testing results of antifouling paint compositions were already recorded (Abd El-Malek, 1972). The formulations were based on a vinyl copolymer and a high content of cuprous oxide; the films were free of fouling and retained their physical integrity after a period of 12 months of continuous immersion. But this result was still not very convincing from a practical point of view, since plastic sheets were used as substrates, whereas what is required by the Egyptian Standard Specifications (1966) is a paint system, applied on a steel substrate, that should provide protection from fouling and rusting for a minimum period of 6 months in local marine environment.

Work recently published (Abd El-Malek and Ghanem, 1977; Abou-Khalil and Ghanem, 1977) revealed that certain compositional factors in both anticorrosive and antifouling paints greatly affect the efficiency of the protective systems.

In anticorrosive coatings of the type containing anodic reaction inhibiting pigments, conclusions were reached that the pigment/binder weight ratio should not be less than 0.9, that 50% by weight of the total pigment should be any of seven inhibitive pigments examined (only three of which are suitable when cathodic protection is used), that the incorporation of the rosin-modified phenolic resins in vinyl binder improves the film properties but impairs the alkali resistance of the paint film, and that under cathodic protection the acidic binder content (acid value 20) should not exceed 10% of the total binder mixture.

In antifouling coatings, 17 different formulations all depending upon cuprous oxide as toxin, a vinyl copolymer as stable binder, and rosin as soluble binder were tested in a raft on steel plates protected from corrosion by formulations selected from those mentioned in the above paragraph. While no single system satisfied the specifications requirements, important conclusions were reached (Abd El-Malek and Ghanem, 1977). To obtain any reasonable period of protection under the prevailing natural conditions, a high Cu_2O content should be supplemented by a high ratio of rosin in the stable binder. Thus, the relatively more successful formulations were those containing 65–55% Cu_2O with 27–36% of the total binder as rosin. It is noteworthy that the above series concentrated on finding out the role played by rosin in coatings containing

high ratios of Cu_2O . The reason for failure of fouling protection for the required period of time was believed to be the use of the wrong type of external plasticizer, which was of a nonhydrolyzable chlorinated paraffin type.

In the present work, two minor modifications in the formulations are performed: one in the anticorrosive and one in the antifouling coating. In the anticorrosive coating, the pigment composition was modified by introducing aluminum powder, which is known for improving the impermeability to moisture and its ability to exclude ultraviolet light. The lamellar pigment particles have the property of laying themselves horizontally and concentrating in the outer part of the paint film. This "leafing" action, which may be due in part to the aluminum stearate film on the particles, serves to lengthen materially the path which the moisture must traverse to get through the film and may eliminate encountered blistering. (Abou-Khalil and Ghanem, 1977).

In the antifouling coating, the nonhydrolyzable chlorinated paraffin plasticizer was replaced in one series by the hydrolyzable plasticizer tritolyl phosphate and in another series by the nonhydrolyzable but swellable plasticizer, polyvinyl methyl ether.

The modifications created remarkable protection improvements which fulfilled the Egyptian Standard Specifications (1962, 1966) requirements for the first time.

Formulations

Anticorrosive Formulations. As it is the aim in the present investigation to examine the value of introducing aluminum powder in the formulation, a typical already examined paint (Abou-Khalil and Ghanem, 1977) was used as reference. Its composition is given in Table I; its anticorrosive function may be ascribed to the presence of high content of the inhibiting pigment basic lead sulfate believed to act as an anodic passivator.

The formulations containing aluminum powder were prepared and arranged in three series. Series 1 (Table II) examines the effect of different binders on the efficiency of the paint. Series 2 (Table III) examines the effect of introducing inhibitive pigment in the aluminum-containing paint. Series 3 (Table IV) examines the effects of some common inert pigments, extenders, and fillers on the paint efficiency.

Antifouling Formulations. The antifouling paints formulated with nonhydrolyzable, hydrolyzable, and swellable nonhydrolyzable plasticizers are given in Tables V, VI, and VII, respectively.

The individual paint compositions are given under serial numbers 1 to 27. With each plasticizer nine formulations were made; each three of them have the same pigment/binder ratio of 3.5, 4, and 4.5. The increase of the pigment/binder ratio was performed mainly through the increase of iron oxide and zinc oxide contents rather than through the increase of the content

Table I. Reference Anticorrosive Formulation without Aluminum

Constituent	Amount
Vinyl copolymer	198
Chlorinated paraffin	22
Rosin-mod. phenolic resin	110
Phenolic resin	110
TOTAL BINDER	440
Basic lead sulfate	280
Iron oxide	56
Talc	84
Barytes	140
TOTAL PIGMENT	560
Pigment:binder	1.3:1
PVC	24

Table II. Anticorrosive Formulations with Aluminum and Different Binders

Constituent	AC no.									
	1	2	3	4	5	6	7	8	9	10
Epoxy resin	37	37	37	37	37	—	—	—	—	—
Hardner	13	13	13	13	15	—	—	—	—	—
Vinyl copolymer	—	—	—	—	—	45	45	45	45	45
Plasticizer	—	—	—	—	—	5	5	5	5	5
TOTAL BINDER	50	50	50	50	50	50	50	50	50	50
Aluminum	50	40	30	20	10	50	40	30	20	10
Talc	—	10	20	30	40	—	10	20	30	40
TOTAL PIGMENT	50	50	50	50	50	50	50	50	50	50
Pigment:binder	1	1	1	1	1	1	1	1	1	1

Constituent	AC no.										
	11	12	13	14	15	16	17	18	19	20	21
Chlorinated rubber	37	37	—	—	—	—	—	—	—	—	—
Plasticizer	13	13	—	—	—	—	—	—	—	—	—
Vinyl copolymer	—	—	22	22	22	22	22	—	—	—	—
Coumarone-indene	—	—	25	25	25	25	25	—	—	—	—
Plasticizer	—	—	3	3	3	3	3	—	—	—	—
Vinyl copolymer	—	—	—	—	—	—	—	22	22	22	22
Phenolic resin	—	—	—	—	—	—	—	15	15	15	15
Rosin-mod. phenolic resin	—	—	—	—	—	—	—	10	10	10	10
Plasticizer	—	—	—	—	—	—	—	3	3	3	3
TOTAL BINDER	50	50	50	50	50	50	50	50	50	50	50
Aluminum	50	30	50	40	30	20	10	50	30	20	10
Talc	—	20	—	10	20	30	40	—	20	30	40
TOTAL PIGMENT	50	50	50	50	50	50	50	50	50	50	50
Pigment:binder	1	1	1	1	1	1	1	1	1	1	1

Table III. Anticorrosive Formulations with Aluminum and Different Inhibitive Pigments

Constituent	AC no.					
	22	23	24	25	26	27
Vinyl copolymer	22	22	22	22	22	22
Phenolic resin	15	15	15	15	15	15
Rosin-mod. phenolic resin	10	10	10	10	10	10
Plasticizer	3	3	3	3	3	3
TOTAL BINDER	50	50	50	50	50	50
Aluminum	30	30	30	30	30	30
Talc	5	5	5	5	5	5
Basic lead carbonate	15	—	—	—	—	—
Basic lead sulfate	—	15	—	—	—	—
Calcium plumbate	—	—	15	—	—	—
Zinc phosphate	—	—	—	15	—	—
Barium metaborate	—	—	—	—	15	—
Basic lead silicochromate	—	—	—	—	—	15
TOTAL PIGMENT	50	50	50	50	50	50
Pigment:binder	1	1	1	1	1	1

Table IV. Anticorrosive Formulations with Aluminum and Different Inert Pigments, Extenders, and Fillers

Constituent	AC no.					
	28	29	30	31	32	33
Vinyl copolymer	22	22	22	22	22	22
Phenolic resin	15	15	15	15	15	15
Rosin-mod. phenolic resin	10	10	10	10	10	10
Plasticizer	3	3	3	3	3	3
TOTAL BINDER	50	50	50	50	50	50
Aluminum	35	35	35	35	35	35
Talc	15	—	—	—	—	—
China clay	—	15	—	—	—	—
Baryte	—	—	15	—	—	—
Titanium dioxide	—	—	—	15	—	—
Micaceous iron oxide	—	—	—	—	15	—
Iron oxide	—	—	—	—	—	15
TOTAL PIGMENT	50	50	50	50	50	50
Pigment:binder	1	1	1	1	1	1

Table V. Antifouling Formulations with Nonhydrolyzable Plasticizer

Constituent	AF no.								
	1	2	3	4	5	6	7	8	9
Vinyl copolymer	127	127	127	115	115	115	104	104	104
Chlorinated paraffin	12.5	12.5	12.5	11	11	11	10	10	10
Rosin-mod. phenolic resin	22	22	22	20	20	20	18	18	18
Ester gum	25.5	25.5	25.5	24	24	24	22	22	22
Rosin WW	33	33	33	30	30	30	27	27	27
TOTAL BINDER	220	220	220	200	200	200	181	181	181
Cuprous oxide	724	645	567	744	664	584	760	679	592
Iron oxide	25	99	103	26	100	106	27	104	110
Zinc oxide	14	19	93	13	19	93	15	19	95
China clay	16	16	16	16	16	16	16	16	16
Additives	1	1	1	1	1	1	1	1	1
TOTAL PIGMENT	780	780	780	800	800	800	819	819	819
Pigment:binder	3.5	3.5	3.5	4	4	4	4.5	4.5	4.5

Table VI. Antifouling Formulations with Hydrolyzable Plasticizer

Constituent	AF no.								
	10	11	12	13	14	15	16	17	18
Vinyl copolymer	127	127	127	115	115	115	104	104	104
Tritolyl phosphate	19	19	19	17	17	17	15	15	15
Rosin-mod. phenolic resin	22	22	22	20	20	20	18	18	18
Ester gum	19	19	19	18	18	18	17	17	17
Rosin WW	33	33	33	30	30	30	27	27	27
TOTAL BINDER	220	220	220	200	200	200	181	181	181
Cuprous oxide	724	645	567	744	664	584	760	679	596
Iron oxide	25	99	103	26	100	106	27	104	111
Zinc oxide	14	19	93	13	19	93	15	19	95
China clay	16	16	16	16	16	16	16	16	16
Additives	1	1	1	1	1	1	1	1	1
TOTAL PIGMENT	780	780	780	800	800	800	819	819	819
Pigment:binder	3.5	3.5	3.5	4	4	4	4.5	4.5	4.5

Table VII. Antifouling Formulations with Swellable Plasticizer

Constituent									
	19	20	21	22	23	24	25	26	27
Vinyl copolymer	127	127	127	115	115	115	104	104	104
Lutonal M40	38	38	38	35	35	35	32	32	32
Rosin-mod. phenolic resin	22	22	22	20	20	20	18	18	18
Rosin WW	33	33	33	30	30	30	27	27	27
TOTAL BINDER	220	220	220	200	200	200	181	181	181
Cuprous oxide	724	645	567	744	664	584	760	679	596
Iron oxide	25	99	103	26	100	106	27	104	111
Zinc oxide	14	19	93	13	19	93	15	19	95
China clay	16	16	16	16	16	16	16	16	16
Additives	1	1	1	1	1	1	1	1	1
TOTAL PIGMENT	780	780	780	800	800	800	819	819	819
Pigment:binder	3.5	3.5	3.5	4	4	4	4.5	4.5	4.5

of the main toxin (Cu_2O) in order not to mask the effects created by the different plasticizers. However, the contents of Cu_2O with respect to total solids were kept at the high copper content of the contact-leaching types of antifouling paints, i.e., 58 to 76%.

Paint Application

Steel plates $30 \times 20 \times 0.1$ cm were cleaned in the usual way until a uniform shiny surface of the metal appeared. Several anticorrosive coatings were applied until a thickness of at least $200 \mu\text{m}$ was obtained, allowing sufficient periods for drying between each coat. The edges were then protected by a two-component epoxy resin. One to two coatings of the antifouling paints were then employed to produce a thickness of at least $80 \mu\text{m}$. The plates were hung in frames each including one or two plates coated with nonantifouling paint to serve as blanks.

Testing

The paint systems were immersed in the testing station (Abd El-Malek and Ghanem, 1975) in Alexandria harbor on May 24, 1976. Periodic visual and biological examination and photographic recording of the condition of the plates were performed. A few days after the examination on Dec 9, 1976, the station was hit by a sudden storm and sank. Much distortion occurred to most of the plates which made continuation of the exposure impossible. However, the rusting condition at that stage was recorded by scraping and visual examination.

The normal leaching rates of the antifouling paints were simultaneously determined and the test is continuing until the present date. The water temperature in the beakers during the test (Abd El-Malek and Ghanem, 1977) was always kept at $24 \pm 1^\circ\text{C}$.

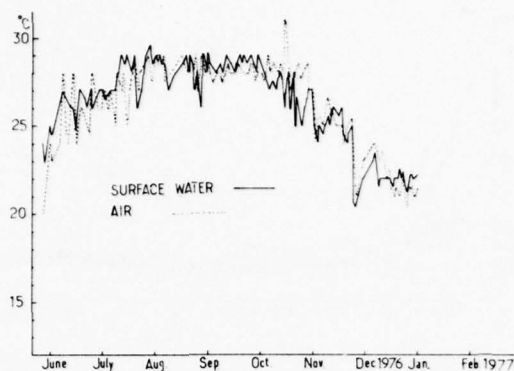


Figure 1. Temperatures.

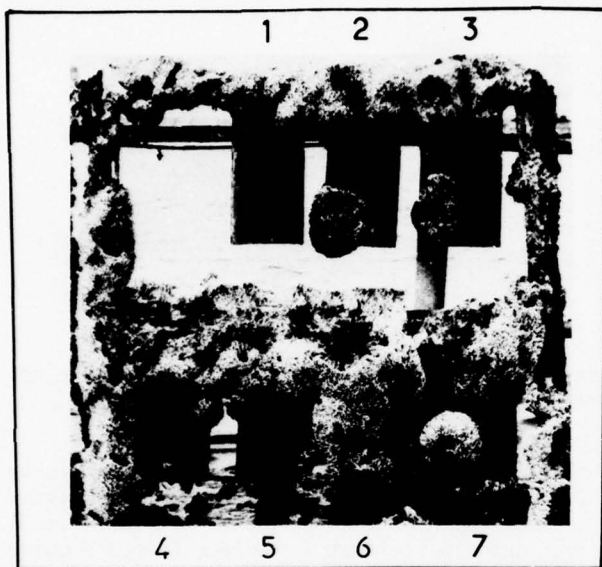


Figure 2. Comparison between Al-containing and Al-free anticorrosive paints: 176 days of immersion; AF no. 25, Table VII; 1, AC no. 29; 2, AC no. 30; 3, AC no. 31; 4, AC no. 32; 5, AC no. 33 (Table IV); 6 and 7, Al-free (Table I).

Results and Discussion

Temperature. The water surface and air temperatures recorded at noon are given in Figure 1. It can be shown that throughout the immersion period, May 24 to Dec 9, 1976, the temperature never went below 20 °C; temperatures of 28 ± 1 °C were prevalent.

Anticorrosive Coatings. Preliminary laboratory corrosion tests gave satisfactory results; there was no indication of superiority of coatings containing aluminum powder over those containing inhibiting pigments without aluminum.

However, the advantages of incorporating aluminum in anticorrosive formulations were revealed in tests in a natural environment. The two bottom plates (right) in Figure 2 were coated with the paint composition given in Table I which contains basic lead sulfate and no aluminum. The rest of the plates were coated with formulations given in Table III which contain aluminum with various inert pigments, extenders, and fillers. The top antifouling composition was no. 25 in Table VII. It can be shown that all anticorrosive formulations containing aluminum helped to keep the surface clean, whereas the anticorrosive paint with basic lead sulfate and no aluminum failed to do so. It can be concluded that the slight rusting

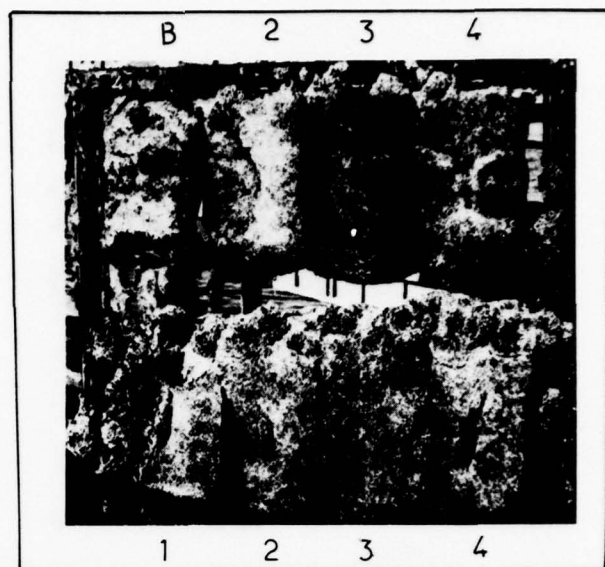


Figure 3. Antifouling paints with nonhydrolyzable plasticizer: 137 days immersion; B, blank plate; 1, AF no. 5; 2, AF no. 3; 3, AF no. 2; 4, AF no. 1. (See Table V.)

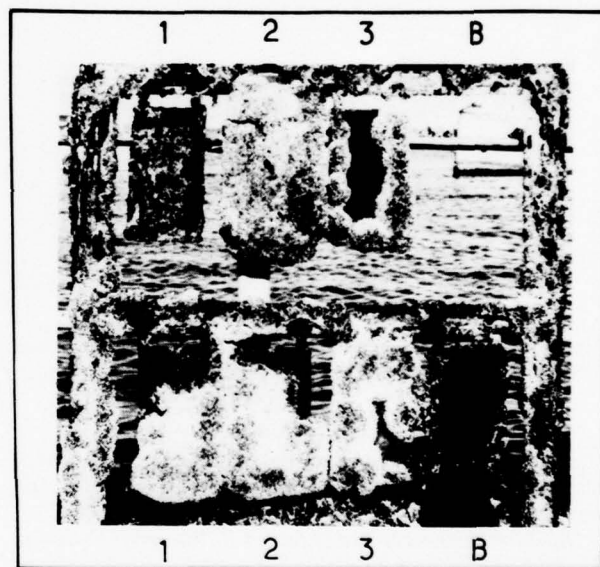


Figure 4. Antifouling paints with hydrolyzable plasticizer: 137 days of immersion; B, blank plate; 1, AF no. 10; 2, AF no. 11; 3, AF no. 12. (See Table VI.)

which has occurred caused damage to the coating system, which in turn led to the heavy fouling shown in Figure 2.

Antifouling Coatings. The behavior of antifouling coatings formulated with a chlorinated paraffin product as plasticizer after 137 days of immersion in the marine testing station is shown in Figure 3. It is clear that the protection efficiency is poor. The attachment and growth of the fouling organisms is so widespread that the failure cannot be attributed to inadequacy of the anticorrosive coating; upon scraping the film after the test, the substrate was found to be almost intact and free from rusting.

The situation is somewhat improved in the series shown in Figure 4 employing the hydrolyzable plasticizer tritolyl phosphate. After 137 days of immersion the plates carried lesser amounts of fouling organisms mainly concentrating on

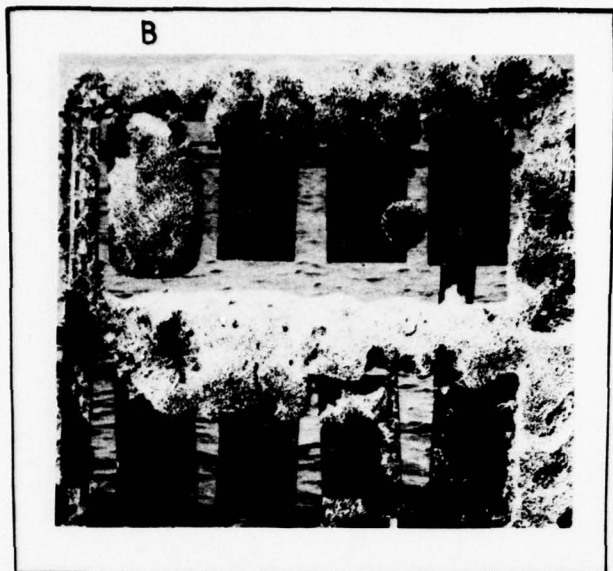


Figure 5. Antifouling paint with swellable plasticizer: 176 days of immersion; B, blank plate; anticorrosives of Table IV; AF no. 25 (Table VII).

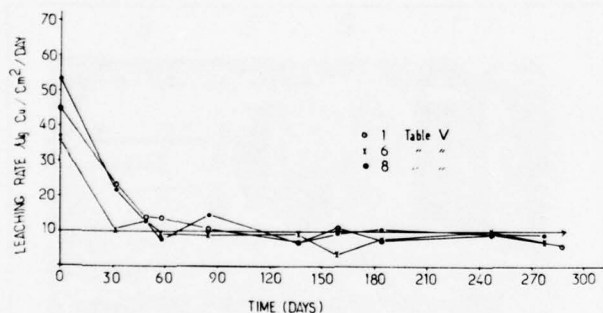


Figure 6. Typical leaching rate experiments of antifoulings with nonhydrolyzable plasticizer.

the rims. It must be noted that the condition of fouling on the plates increased remarkably after the third month of immersion.

Much better results are obtained in the series shown in Figure 5 employing a swellable but nonhydrolyzable plasticizer. After a longer period of immersion, 176 days, the coating system is completely intact and fouling is either absent or at a minimal level. Any fouled spot could be ascribed to some mechanical damage which occurred accidentally during lifting and reimmersing the testing racks for periodic examination.

Leaching Rate Experiments. Laboratory support to the above findings is provided from leaching rate experiments carried out simultaneously on the same paints (AF-No 1-27) tested in the raft. As already stated, the raft sank about 7 months after sample exposure; however, the laboratory leaching rate test is operational to the present date and will, hopefully, go on until the end.

Figure 6 records the leaching behavior of copper for 10 months (last reading on March 9, 1977) from paints prepared with chlorinated paraffin plasticizer. It can be shown that while the leaching of copper is satisfactory during the first 2 months, it sinks quite rapidly afterward to values of $10 \mu\text{g}/(\text{cm}^2 \text{ day})$ or less, which is insufficient for a fouling rich environment such as that of the present investigation.

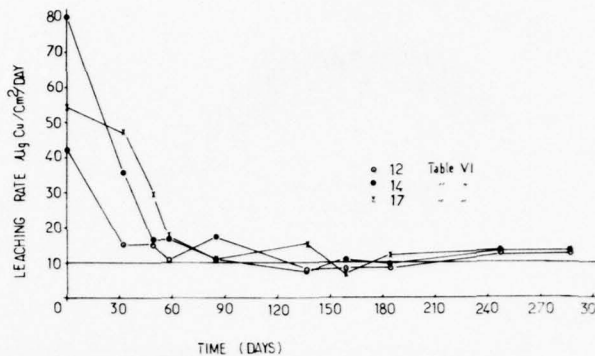


Figure 7. Typical leaching rate experiments of antifoulings with hydrolyzable plasticizer.

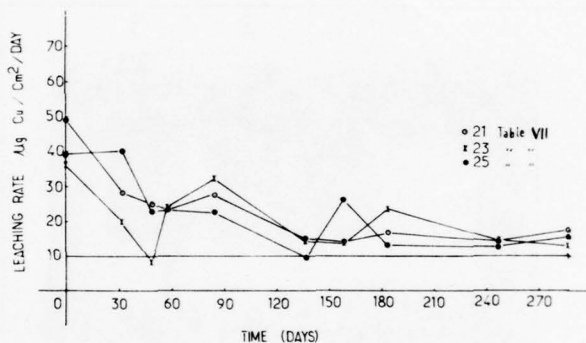


Figure 8. Typical leaching rate experiments of antifoulings with swellable plasticizer.

Figure 7 records the leaching behavior of copper, for the same period of time, from paints also selected at random from the series prepared with tritolyl phosphate as plasticizer. It can be shown that although the leaching of copper is higher and is extended to a period of about 3 months, the leaching that follows is characterized by values very near the critical $10\text{-}\mu\text{g}$ line.

The influence of the swellable plasticizer on the leaching rate is shown in Figure 8 which records high values for a much extended period of time; leaching rates higher than $15 \mu\text{g}/(\text{cm}^2 \text{ day})$ are recorded 10 months after continuous immersion in tanks in the laboratory. The trend of the curves promises longer protection periods.

The differences between the leaching behavior of three paints selected at random, each containing one of the three different plasticizers, are clearly represented in Figure 9. The hydrolyzable plasticizer allows initially higher leaching rates than the two other plasticizers but only for a period of 2 to 3 months after which the leaching rate falls to somewhat critical values which might allow scattered settlement. The nonhydrolyzable plasticizer, on the other hand, does not allow sufficient leaching after a period of not more than 1 or 2 months; an otherwise proper formulation is thus wasted, particularly under prevailing warm and fouling-rich conditions. The formulation which gives optimum behavior is that containing an unconsumable but swellable plasticizer which allows opening of the structure without unnecessary loss of active ingredient; formulations with Lutonal exhibited a greenish appearance which increased in intensity along the leaching rate experiment. This is most probably basic copper carbonate retained in voids created as the plasticizer swells.

Conclusion

Raft testing in a natural environment which combines

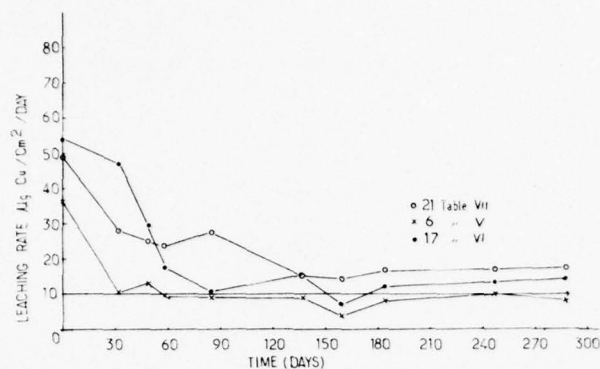


Figure 9. Comparison between leaching rates of antifoulings with different plasticizers: X, with nonhydrolyzable AF no. 6; ●, with hydrolyzable AF no. 17; ○, with swellable AF no. 21.

rather severe climatic conditions with nontoxic pollution provides valuable information as to the efficiency of underwater protective systems.

In anticorrosive paints, incorporation of lamellar aluminum in formulations based on a vinyl copolymer as binder provides better protection than when inhibiting pigments of the anodic passivation class are used without aluminum.

In antifouling paints, a swellable but nonhydrolyzable plasticizer is superior to both nonhydrolyzable and hydrolyzable counterparts in regulating toxin release and allowing retention of surface copper in the form of basic copper carbonate.

Acknowledgment

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(3)

Preparation and Testing of Antifouling Coatings
Based on Tributyltin Fluoride
Proceedings of a Discussion of Corrosion Control
by Coatings. November 13-15, 1978. Lehigh University
Bethlehem, Pennsylvania, U.S.A. Pages VE1- VE 10
By
N.A. Ghanem and M.M. Abd El-Malek

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'a misplacement', sorry.*

**ANTIFOULING COATINGS PART I. PREPARATION AND TESTING OF
ANTIFOULING COATINGS BASED ON TRIBUTYL TIN FLUORIDE**

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ABSTRACT

In view of the limited period of protection of cuprous oxide-based antifouling coatings in fouling-rich regions and the danger of copper accumulation in waters and sediments in semi-enclosed areas, need for longer protection periods with less polluting effects has emerged. In this paper tributyltin fluoride is used as alternative to cuprous oxide in preparation of a variety of paints meant for fouling resistance for long periods. The results of testing in natural environment of high fouling intensity are very promising with respect to animal organisms but not very much so with respect to plant fouling.

INTRODUCTION

In a previous publication (1) dealing with antifouling coatings depending on vinyls as binders and cuprous oxide as toxic pigment, it was determined that the maximum period of protection in fouling-rich regions was thirteen months. It was claimed that research should be directed to areas where other binder systems are used or higher efficiency toxins may supplement or replace cuprous oxide. This trend is prompted by recent investigations (2) in which copper at two orders of magnitude higher than the natural limit was determined in the waters and sediments of the Suez Canal. This threatening level was attributed - solely - to copper leached out from ships traversing the international pathway at a rate estimated at 3000 vessels per month. The phenomenon of increased copper levels was also observed in other places such as the harbors of Antibes, La Pallice and La Rochelle in South France (3). The high copper concentrations were attributed to the great number of pleasure boats which use copper and cuprous oxide antifouling coatings. High copper concentrations were also determined in the waters of the docking areas of San Francisco Bay (4). The same author found copper contents in abundant marine algae, Ulva sp. ranging from 10.6 to 53.4 $\mu\text{g/g}$ tissue (dry weight). Further alarm was provided by Disalvo (5), where the effect of copper on the survival and functioning of the lower - but most important organisms -, the bacteria, was examined. The results indicated variable susceptibility of bacteria to the presence of copper and suggested the possibility of cumulative synergistic effect of heavy metals on bacterial motility. It was estimated that 5000 tons of copper are released yearly from copper-based antifouling coatings in the oceans and seas of the world (6).

In the present investigation the binder mixture - based essentially on a vinyl copolymer - was kept the same, while cuprous oxide was replaced entirely by one of the recently developed organotin compounds. Trialkyl- and triaryltin compounds have been gaining ground since their fungicidal effects were discovered in 1954. They were recommended for antifouling applications because of their slow but effective release, because of the long periods of protection of as much as two years and because they do not accelerate corrosion. An instance of protection against fouling for 92 months has been documented (7) where tributyltin compounds were included in a thick rubber sheet.

The type of plasticizer for the vinyl binders was shown to play an important role in antifouling coatings depending on cuprous oxide as toxic ingredient (1); its chemical composition controls the leaching rate of copper and hence the prevention of fouling in long-term environmental immersion. The present investigation includes the use of three different commercial plasticizers - hydrolyzable, nonhydrolyzable and nonhydrolyzable but swellable plasticizer - to examine their role in conjunction with tributyltin fluoride as toxic ingredient.

While it was hoped to conduct the environmental testing for much longer period, the test was terminated after 211 days due to a sudden storm which sank the raft. However, the photographic recording of the last inspection could provide evidence of further protection periods.

MATERIALS

The vinyl copolymer was Laroflex MP 35 from BASF AG, Ludwigshafen, Germany. The plasticizers were: chlorinated paraffin (nonhydrolyzable) n 50 from Farbwerke Hoechst AG, Germany, tritolyl phosphate (hydrolyzable) and polyvinyl methyl ether (nonhydrolyzable but swellable) Lutonal M 50 from BASF AG. The modifying resins were ester gum; a product of Carless Capal, England, and a phenolic resin which was Wresnyl 265, a product of Resinous Chemicals, England. Thixtrol ST, a hydrogenated castor oil used as antissettling agent was also obtained from BASF, AG. Tributyltin fluoride was obtained from Berk, Co., Ltd., England. Titanium dioxide was of the rutile type, a product of Titangesellschaft, AG, West Germany. Iron oxide was of the type 130 F from Farbwerke Bayer, AG, Germany. China clay was obtained from English China Clays, Sales Division, England. Suitable mixtures of xylene, white spirit (145 - 185°C), butyl acetate and butanol were used as solvents.

EXPERIMENTAL

Paint Preparation

Formulations in the amount of 300 g each were prepared by mixing the selected amounts of ingredients. The mass was matured and then dispersed in a centrifugal ball mill. The paints were diluted to the application viscosity using a suitable blend of solvents, filtered twice, and stored in tins with tight lids in a cool place. The storage time before application ranged between 2 and 4 weeks; the paints were free from sediments or any other defects after several months of storage.

Test Panels

Sheets, 3 mm thick, of pigmented impact-resistant polystyrene were cut to panel dimensions of 20 x 15 cm, the edges were tapered and the surfaces were coated with a thin layer of an epoxy paint, left to dry and then roughened with sandpaper. The use of polymer panels avoided corrosion interference and complications of incomplete compatibility with the anticorrosive layer.

The panels were coated in duplicate, front and back, with two successive coats allowing an interval of 6 hours for drying between the two coats; the average film thickness was $90\mu\text{m} \pm 10\mu\text{m}$. Particular care was paid to the edges to eliminate pores and weak points.

The coated panels were connected to boat-like cages with nylon threads through holes bored in the panels. Each composition was represented by two panels; one placed in a vertical position and the other at 60° to the horizontal.

Environmental Exposure

The cages were submerged in the test area of the raft (8) in Alexandria, Egypt (eastern harbor) on 24 May at a depth of about 150 cm from the surface. Periodic visual and biological examination and photographic recording of the condition of the panels were performed. The region is known for its abundant fouling organisms almost all the year round; there are reasons to believe that the rate of growth of most foulers has doubled since the extensive survey concluded by Ghobashy (9) in 1975. Periodic testing of water salinity, temperature, and pH was performed.

RESULTS AND DISCUSSION

Paint Compositions

Ten paint compositions were prepared with a common binder mixture containing mainly a neutral vinyl copolymer. A slight acidity was obtained by a small amount of ester gum resin (acid number 3-5 mg KOH/g) and some improvement of hardness was imparted by a small content of a phenolic resin. A traditional constituent in antifouling coating, rosin, was absent from all formulations. It was established long ago that rosin plays an important role in the performance of both soluble-matrix and contact-leaching copper antifouling coatings. In trialkyl- or triaryltin compounds, the mechanism is believed to be one of slow-release which does not depend on the dissolution of rosin but rather on migration of a particle of the compound from the interior of the coating to its surface and then to the water (10).

Tributyltin fluoride was introduced in the formulations in four different amounts, namely, 15, 20, 25 and 30% by weight of the total dry film. Values in some of the literature available (11, 12) on tributyltin fluoride antifouling coatings range between 16 - 20%; values of 30 - 40% are given in other literature (13) but these amounts were considered to be impractical. The wide range used in the present work was designed for the severe fouling conditions at the test site. Talc and China clay were included in substantial amounts not only for improving paint properties but also for their favorable control of the rate of release of the toxic ingredient. The coating compositions are given in Table (1) which also includes a calculation of the total pigment volume concentration and the toxic (pigment) volume concentration.

Test Results

All coatings were completely intact and free from fouling at the end of the first two months of immersion. A general feature was the formation of slime and attachment of slight algal growth. Only a few barnacles were observed at the edges and around the holes of the panels due to bare points and some detachment of the coating during manipulation.

Table (1)
Dry Film Composition of Antifouling Coatings

AF. No.	1	2	3	4	5	6	7	8	9	10
Constituent	1	2	3	4	5	6	7	8	9	10
Vinyl Copolymer	15	15	15	15	17	17	17	16	16	16
Polyvinyl Methyl Ether	4.5	4.5	4.5	4.5	--	--	--	--	--	--
Chlorinated Paraffin	--	--	--	--	1.7	1.7	1.7	--	--	--
Tritolyl Phosphate	--	--	--	--	--	--	--	2.5	2.5	2.5
Phenolic Resin	3	3	3	3	3.3	3.3	3.3	3.2	3.2	3.2
Ester Gum	2.5	2.5	2.5	2.5	3	3	3	3.4	3.4	3.3
TBTF	15	20	25	30	20	25	30	20	25	30
Iron Oxide Red	14	14	14	14	14	14	14	14	14	14
Titanium Dioxide	20	20	20	20	20	20	20	20	20	20
Talc	15	10	5	--	10	5	--	10	5	--
China Clay	11	11	11	11	11	11	11	11	11	11
PVC	58	60	61.6	63.0	60.5	61.9	63.4	60.2	61.9	63.3
TOXIN VOLUME CONC N	24	31	37.3	43	31.3	37.4	43.2	31.3	37.4	43.1

From the beginning of the third month until the test was terminated, the intensity of the slime film on all plates was moderate but the film tended to be thicker on coatings with lower contents of the tin compound. No serious attack of the test panels by barnacles, tube worms or other foulers was observed throughout the whole period of immersion of 211 days. Little scattered settlements took place at the edges only.

Photographic recording of the test is shown in Fig. (1). The great contrast between the cleanliness of the coated panels and heavy fouling on the supporting cage is clearly demonstrated. The latter carried such heavy loads of barnacles and tube worms, reaching 12 to 15 cm in thickness at the last inspection, that parts of the test panels area were hidden behind the intensive growth. Continuation of the test would have left very little room for comparison between the individual formulations for their relative long-term efficiency because of encroachment of fouling. A new design of supporting frames which provided larger space between the test panel and other objects was developed and used (1).

The test period (211 days) was either too short to provide differentiation between the plasticizer type or the protective function in the case of organotin compounds was independent of the chemical nature of the plasticizer. These results are in contrast to cuprous oxide formulations where antifouling function was lost much earlier in the aforementioned period when a nonhydrolyzable plasticizer was used (14). The second postulation is more plausible and supports the view that the mechanism of protection by organotin formulations depends on the ability of the toxic particle to diffuse from the interior of the film to its surface. This diffusion is controlled by the texture and configuration of other components of the coating (15) rather than on the swellability of the plasticizer (1) or the solubility of other components like rosin.

One of the disadvantages of slow-release organotin formulations is their very short range of protection; the repellancy to fouling larvae takes place in the vicinity of the surface only in contrast to copper formulations which leach out a soluble toxic layer which has its effect over a much longer range. Full protection of the edges and corners was therefore much more difficult in organotin formulations than in their copper counterparts.

Another drawback is the ineffectiveness of organotin formulations on plant foulers relative to copper formulations. Although brown algae was detected in the present series, serious plant fouling did not appear because the experiment was terminated before the season of plant fouling which begins early in the spring; plant fouling was detected and characterized in a later series (16). One of the solutions of this drawback is to use combined cuprous oxide-organotin formulations.

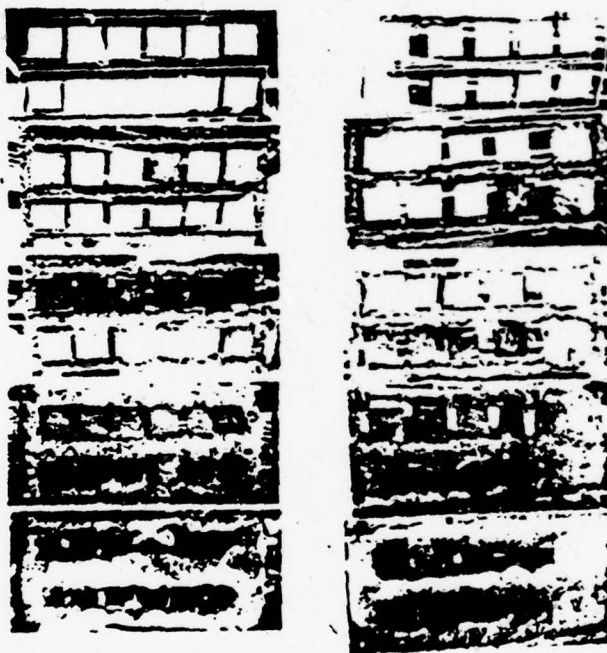


Figure 1. Environmental testing of tributyltin fluoride antifouling coatings. Samples are identified in Table I. From left to right they are: First set: 5, 6, 7, 8, 9, 10; Second set: 4, 3, 2, 1, blank. The row are identified as follows: 1st row, appearance at start on May 24; 2nd row, after 61 days; 3rd row, after 88 days; 4th row, after 139 days; 5th row after 201 days.

CONCLUSION

Vinyl binder coatings containing 15 - 30% by weight tributyltin fluoride are effective antifoulants and satisfy standard specification (18) of six months protection in natural environment. They function by a slow-release mechanism which is independent of the presence of a soluble ingredient, and thus their effective life-time is prolonged in comparison with compositions based on cuprous oxide as toxin and rosin as soluble ingredient. A further advantage of the formers lies in their less hazardous effects on marine ecology, particularly in harbors and narrow water pathways. The economy seems favorable with increasing production of organotin compounds.

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DOCUMENT

(4)

Preparation and Testing of Antifouling Coatings

Based on Triphenyltin Fluoride

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**ANTIFOULING COATINGS PART II. PREPARATION AND TESTING OF
ANTIFOULING COATINGS BASED ON TRIPHENYLTIN FLUORIDE**

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ABSTRACT

Antifouling paints were prepared using a vinyl copolymer as main binder and triphenyltin fluoride alone as the toxic ingredient. The paints were tested in a heavily infested marine locality with the aim of throwing light on the following questions pertaining to long-term protection: 1. The function of the nature of the organic residue in the organotin compound. 2. The optimum concentration of the organotin compound in the formulation. 3. The contribution of the classical soluble ingredient, rosin, in slow-release formulations employing an organotin compound for fouling prevention, 4. The role of the pigment extender in the proper functioning of the antifouling coating.

Photographic follow-up of the condition of test panels during 238 days of continuous immersion allowed decisive conclusions with respect to some of the aforementioned questions which should help in producing modern, economic, durable and less hazardous organotin antifouling paints for use in fouling-rich regions.

INTRODUCTION

Notwithstanding current attempts to create nontoxic antifouling coatings (1), all commercial antifouling coatings until the present day depend on the development of a toxic laminar layer capable of killing or repelling the larval attachment. Among the thousands of toxic compounds in different classes of organic, heterocyclic and inorganic compounds, copper compounds (mainly cuprous oxide) meet most of the requirements and have dominated the scene in commercial formulations (2) for many years for reasons stated in a previous publication (3). However, cuprous oxide-based paints began to lose grounds in recent years for compositions based on certain organotin compounds, alone or mixed with cuprous oxide. The reasons were a combination of factors which, although invisible in the commercial literature, are possible to trace in independent research efforts. One of the reasons is inherent, depending on the necessity of consumption of copper from the film at a rate not less than $10\mu\text{g}/\text{cm}^2/\text{day}$ irrespective of the mechanism, and thus connecting the protection period to the full depletion of the poison store or the clogging the pores through which the poison may pass. In a recent publication, the period of protection of a highly recommended class of cuprous oxide-based antifouling compositions in a region of intensive fouling was set at a maximum of 13 months (3). Another reason may be extracted from hydrological studies where alarming copper concentrations were found in the waters of some harbors in the south of France (4), in organisms in the waters of San Francisco Bay (5) and in the waters and organisms in the Suez Canal (6).

The above problems have been solved, at least in part, by the advent of organotin compounds and polymers. One of these compounds, *bis*-tributyltin oxide, a liquid which received considerable success at one time, was however banned from use in some countries. Among the rest of the organotin compounds tributyltin fluoride (TBTF) and triphenyltin fluoride (TPTF) are outstanding until the present time for being solids which can be incorporated at desired ratios, for their slight but effective solubility in sea water, and for their reasonable dissolution in common paint solvents. In contrast to matrix dissolution or contact leaching mechanism of cuprous oxide coatings, the mechanism in organotin coatings is believed to be one of slow-release depending on the migration of toxic particles from the interior of the film to its surface and then to the water (7), thus allowing a much longer period of protection (8). Much higher toxic efficiency of organotin compounds compared with cuprous oxide, estimated at five times, is not only an economic advantage but also a non-pollution factor especially as most organotins are believed to be eventually converted in sea water to inorganic tin compounds such as the carbonate which, contrary to other metal inorganic compounds like those of copper arsenic and mercury, are non-toxic (9).

In a previous publication (10), formulations based entirely on tributyltin fluoride for toxicity were prepared and tested in heavily infested natural environment (11, 12). Their efficiency against plant fouling was doubtful in view of absence of flourishing algal growth, i.e., spring and early summer, from the total test period. Otherwise, it was concluded that coatings containing 15 - 30% by weight of TBTF are effective and satisfy standard specifications (13) of keeping the surface completely clean for

6 months in a natural environment.

In the present work, TBTF was replaced by TPTF and the immersion period was extended to include the season of extensive plant fouling. The aim was to throw more light on the nature of the mechanism of fouling prevention; TPTF being claimed to be more stable to heat, U. V. light and hydrolysis than its tributyl counterpart and less soluble in sea water (14). The studies are supplemented by a series employing graded amounts of the sea-water-soluble ingredient, rosin, which helps release in copper formulations. A series is also devoted to examining the role of 6 different pigment extenders, the particle size, shape and texture of which are believed to contribute in controlling the mobility of the toxic particle while traversing the film bulk to its surface.

MATERIALS

A full description of all materials except TPTF and the pigment extenders was given in Part I. (10). TPTF was obtained as fine powder from M & T Chemicals Inc. (Subsidiary of American Can Company), Rahway, New Jersey, U.S.A. China clay was obtained from English China Clays Sales, England. The other pigment extenders were obtained as trade samples through BASF, AG., West Germany; their sources were not given.

EXPERIMENTAL

The Paints

Three groups of a total of 12 antifouling compositions based mainly on a neutral vinyl copolymer were prepared. Group I comprised 3 compositions containing graded amounts of TPTF which were 10, 15 and 20% by weight of the dry film, while the binder, pigment and extenders were fixed except the talc from which content the toxin was substituted. The formulations are given in Table (1).

Group II consisted of 3 compositions differing only in the rosin content which was present in graded amounts of 15, 30 and 45% by weight of the binder mixture, while the toxin and other ingredients were kept constant. The compositions of Group II paints are shown in Table (2).

Group III comprises 6 compositions in which the contents of the nontoxic pigments were kept the same while a different pigment extender was used in each formulation, i.e., six extenders were incorporated in this group, namely, talc, china clay, barytes, asbestine, lithopone and magnesium trisilicate. The paint compositions (dry film) are shown in Table (3).

Table (1)
Compositions of Group I Paints.
The Effect of TPTF Content.

AF No. Constituent	1	2	3
Vinyl Copolymer	15	15	15
Polyvinyl Methyl Ether	4.5	4.5	4.5
Phenolic Resin	3	3	3
Ester Gum	2.5	2.5	2.5
Triphenyltin Fluoride	10	15	20
Iron Red	14	14	14
Titanium Dioxide	20	20	20
Talc	20	15	10
China Clay	10.9	10.9	10.9
Additives	0.1	0.1	0.1

Table (2)
Compositions of Group II Paints.
The Effect of the Rosin Content.

AF No. Constituent	4	5	6
Vinyl Copolymer	13.75	11.50	9.00
Polyvinyl Methyl Ether	4.50	3.50	2.75
Phenolic Resin	3.00	2.50	2.00
Rosin	3.75	7.50	11.25
Triphenyltin Fluoride	15	15	15
Iron Red	14	14	14
Titanium Dioxide	20	20	20
Talc	15	15	15
China Clay & Additives	11	11	11

Table (3)
Compositions of Group III Paints.
The Effect of the Pigment Extender.

AF. No. Constituent	7	8	9	10	11	12
Vinyl Copolymer	15	15	15	15	15	15
Polyvinyl Methyl Ether	4.5	4.5	4.5	4.5	4.5	4.5
Phenolic Resin	3	3	3	3	3	3
Ester Gum	2.5	2.5	2.5	2.5	2.5	2.5
Triphenyltin Fluoride	15	15	15	15	15	15
Iron Oxides red	14	14	14	14	14	14
Titanium Dioxide	20	20	20	20	20	20
Talc	--	--	25.9	--	--	--
China Clay	25.9	--	--	--	--	--
Barytes	--	25.9	--	--	--	--
Asbestine	--	--	--	25.9	--	--
Lithopone	--	--	--	--	25.9	--
Magnesium Trisilicate	--	--	--	--	--	25.9
Additives	0.1	0.1	0.1	0.1	0.1	0.1

Paint Preparation

Laboratory specimens of 300 g. each were prepared. The pigments were first mixed and then the binder mixture in part of the solvents mixture was added and the whole was homogenized in a centrifugal ball mill. The toxic agent TPTF was included in the pigment mixture from the beginning. When a fineness of the grind of less than $10\mu\text{m}$ was reached using a Hegemann gauge, milling was stopped. The paints were diluted to the application viscosity using the same blend of solvents, filtered twice and stored in tins with tight lids. The storage time before application ranged from 2 to 4 weeks.

Panel Preparation

The test panels were cut to dimensions, $30 \times 17\text{cm}$, from pigmented, impact-resistant polystyrene sheets, the edges were tapered and the surfaces were coated with an epoxy paint, left to dry and then roughened with sand paper. The epoxy layer served as protection against attack of the substrate by the aromatic solvents of the antifouling paint thus avoiding defects (cracks) in the dry antifouling film. The use of a polymer substrate avoided corrosion and rust problems and probably complications of incomplete compatibility with the anticorrosive layer.

Each composition is represented by two surfaces, front and back, of one panel hanging in a vertical position. Two successive coats were applied to each face at intervals of 8 - 14 hours to allow drying, the total average film thickness was $90\mu\text{m} \pm 10\mu\text{m}$. Particular care was paid to avoid pores and weak points at edges.

The coated panels were supported in the test stand by nylon threads through holes bored in the panels. The present testing stand shown in the figures is a modification of a previous one (10) that avoids encroachment of fouling masses from the ribs of the stand to the testing panels.

Raft Testing

The stands were submerged in the test area of the floating station (11) in eastern harbor of Alexandria, Egypt, on September 30, 1977 at a depth of 150 cm from the surface. Periodic visual and biological examination and photographic recording of the condition of the panels were performed. The region is known for its abundant fouling organisms almost all the year round; there are reasons to believe that the rate of growth of most foulers, especially the tube worms, has doubled since the extensive survey concluded by Megally (15) in 1970, and by Ghobashy in 1973 (published in 1976) (12).

RESULTS

The following results were derived from examination of the test panels at intervals during the immersion period.

Group I. Paints:

1. The antifouling efficiency was directly proportional to the triphenyltin fluoride content in the composition. There were no remarkable differences in the condition of the surfaces of the three compositions during the initial period of 120 days immersion except for a few individual attachments of barnacles and tube worms at the edges of compositions 1 and 2 (see collective Fig. (1)). Aggressive growth of heavy colonizers from the ribs of the stand to the interior of these two panels covering about 50% of the surface areas was observed in the last inspection. Different foulers were detected, namely, barnacles, tube worms, ascidians and bryozoans, and these formed a thick layer of about 10 to 12 cm.

2. Thick slime films consisting of bacteria, diatoms and detritus materials formed over all the panels. Algal growth constitutes a great part of the slime film. Brown algae were detected in the early period of immersion; three species have been recorded Histrochylum pastulatum, Jania subenus and Corallins sp. It was reported (12, 15) that the above individuals are present at the testing site all year round. During the winter months and in the beginning of spring, heavy green algal growth was abundant; the most predominant species were: Ulva Lactuea and Enteromorpha clathrata. It is observed that the attachment of the organisms begins at the upper parts of the panels and spreads downwards to the lower edges. The thickness of the slime film is dependent upon the toxin content in the composition. Three levels in the slime intensity can be differentiated ranging among heavy, moderate, and moderate to slight. The rate of slime formation on the testing panels can be arranged as follows: $AF_1 > AF_2 > AF_3$.

Group II Paints:

The three compositions (4, 5, 6) with increasing rosin contents are represented by three panels. The following results were derived from the condition of the panels during the period of test (see Fig. (1)).

1. The higher the rosin content, the thicker the slime film that formed and the heavier the attack by plant fouling.

2. The antifouling efficiency for animal foulers was generally diminished mainly due to the presence of rosin in the compositions. Composition 2 of group I which contains the same toxin content, 15% TPTF, in the dry film but no rosin has better efficiency than any member of group II. The presence of rosin accelerated the formation of heavy slime films and reduced the slow release of toxin particles and thus encouraged the settlement of foulers, namely, barnacles on the heavily slimed surfaces (9). The condition of surfaces of composition 4, which contains the lowest amount of rosin, was nearly similar to that of composition 2 with no rosin but smaller TPTF content. Fig. (3) shows the heavy attack by plant fouling after 177 days of immersion.

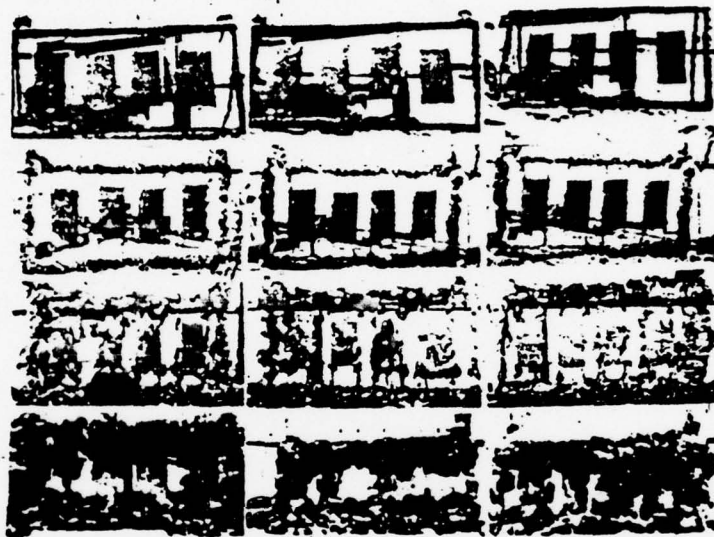


Figure 1. Collective view of panels after immersion times of 34 days (row 1), 120 days (row 2), 177 days (row 3), and 238 days (row 4). Samples are arranged in column form and from left to right are in the order, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1. Compositions of coatings are given in Tables 1, 2, and 3.

Group III Paints:

This group includes 6 compositions each containing only one extender. The extenders used are included in the compositions in Table (3). Fig. (1) shows clear differences between the 6 antifouling systems which are unified in all constituents except the type of the pigment extender. Good antifouling efficiency was obtained with compositions 7 and 11 which contain China Clay and lithopone, respectively. The rest of the formulations have efficiencies ranging from moderate to low. The antifouling efficiency can be arranged in the following order:

AF₇ (China clay) > AF₁₁ (lithopone) > AF₁₂ (Mg trisilicate) > AF₁₀ (Asbestine) >
AF₈ (barytes) > AF₉ (talc).

DISCUSSION

Triphenyltin fluoride is one of the most promising organotin compounds to be used in antifouling coatings. It provides good resistance to attachment of many fouling organisms specially the serious kinds, namely, barnacles and tube worms, but it fails to prevent plant attachment, mainly, algae.

Vinyl-based antifouling composition should employ triphenyltin fluoride in amounts near 20% by weight in the dry film; lower contents make the formulation parameters more critical to proper content of each of the other constituents employed. In contrast, systems based on Cu₂O with as high contents as 80% are easier to study. In a recent system employing 97% Cu₂O and polyisobutylene rubber as a sole binder (16) the role of the other constituents disappears completely but the poor adhesion on substrate of anti-corrosive layer provides difficulties.

Compositions 1, 2 and 3 conserve on the use of TPTF since these contain 10 to 20% by weight. It might have been preferable to increase the content to 25% or more in order to obtain maximum performance in environments of severe and serious fouling conditions. Composition 3, containing 20% TPTF, was successful in controlling serious fouling attack for a period of 8 months (see Fig. (2)), but there is no evidence of protection for longer periods, similar to the compositions which resisted attachment in panel exposure in Biscayne Bay, Miami, Florida, for two years. Such efficient compositions may be applied to idle ships of limited activity which remain still in warm, fouling-rich waters for long periods (17), like naval ships in time of peace and certain kinds of freighters which spend many weeks in ports; while compositions of less toxin content, i.e., 15 ± 3% TPTF may be used on vessels staying in ports for short periods only, such as tankers or ships which should go into dry-dock every 6 or 9 months for periodic maintenance.

Introduction of rosin in antifouling coatings is of great importance for its effectiveness in maintaining adequate release of toxins. It was established long ago that rosin plays an important role in the performance of both soluble matrix and contact-leaching copper antifouling coatings which contain mainly Cu₂O. In the case of systems based on organotin compounds the stand is different due to the wide difference in the physical and chemical properties of organotin antifoulants. For example,



Figure 2. The appearance of Group I coatings after underwater exposure for 238 days. From left to right samples are 1, 2, and 3.

the most common organotin compounds, namely, tributyltin oxide (TBTO), TBTF and TPTF have different solubilities in sea water of pH 8.2, 51.4, 6.0 and 0.7, parts per million, respectively. It is expected that each organotin compound has a certain behavior either in the wet paint or as painted films in contact with sea water. According to the little literature available no sharp conclusions on their mode of action can be derived. According to Bennett and Zedler (18) good antifouling efficiencies of paints containing TBTO may be obtained with binder/rosin ratios equal to or greater than 1, but also with rosin-free paints. In another investigation (19) by De la Court and De Vries on the leaching of several organotin compounds from paints based on chlorinated rubber and vinyl binders, the toxin release appeared to be almost independent of rosin content but they could not establish a clear mechanism of leaching due to difficulties in the analysis of the organotin compounds, especially in sea water. Recent studies of effect of rosin on the release of TPTF from vinyl systems (20) showed that the more effective compositions are those containing rosin in an amount equal to 66% by weight of the binder mixture or 24% of the total dry paint film.

The results of group II paints contradict the above findings; as the rosin content in the composition increased, the antifouling efficiency is reduced. Fig. (3) illustrates that the largest unfouled area is on panel No. 4 of the least rosin content. This may be due to deficiency of toxin concentration in the heavy slime layer adhering to the paint film. In view of the much greater dissolution of rosin than TPTF from these compositions in basic (pH 8.2) sea water, the former would preferentially react with calcium and magnesium salts forming insoluble soaps which would be deposited in the slime film along with other organic and inorganic detritus material and would interfere with the release of TPTF from the coating surface to the water. Any reaction between rosin and the hydrolysis product of TPTF, such as the hydroxide or the carbonate, would give organotin soaps of unknown toxicity. This is not the case in formulations containing near stoichiometric amounts of rosin and cuprous oxide, where readily formed copper rosinate contributes to the toxicity with ionic copper liberated through the catalytic action of chloride ion in sea water; both copper sources help in reducing the intensity of the slime film or keep it enriched with toxins at a level which prohibits fouling.

The results of exposure of compositions of group III (see Fig. (4)) employing six different pigment extenders draws the attention to the importance of the role played by the morphology, particle size, shape and texture of a major component in antifouling coatings depending on a slow-release mechanism. There is evidence that China clay contributes to efficient release and helps in maintaining a clean surface for long periods. On the other hand, talc and barytes should be avoided in TPTF slow-release formulations. Other pigment extenders were ranked on a scale between 10 for China clay and 4 and 5 for talc and barytes, respectively. Selection of the best pigment extender needs further study.



Figure 3. The appearance of Group II coatings after underwater exposure for 177 days. From left to right samples are 4, 5, and 6.



Figure 4. The appearance of Group III coatings after underwater exposure for 238 days. From left to right samples are 7, 8, 9, 10, 11, and 12.

CONCLUSION

Long-term raft testing in marine environment of intensive fouling provides practical data of great importance to producer and user of antifouling paints. Moreover, light can be thrown on the mechanism of function by proper design of the series investigated. In the above work, the level of incorporation of the active component, TPTF, has been set at 20% by weight and the change of the organic moiety in organotin fluorides has no role in controlling plant foulants. Contrary to previous belief, incorporation of rosin was found to be of disadvantage to organotin formulations depending on slow-release. Among the pigment extenders used, China clay and lithopone were the best for efficient long-term release; talc and barytes were the poorest.

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By

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Limit of Protectability Of Vinyl-Cuprous Oxide-Based Anti-Fouling Coatings In Fouling-Rich Regions

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Three sets of a total of 20 individual well-designed anti-fouling paints were tested in the fouling-rich Alexandria (Egypt) eastern harbor waters. More or less the same constituents were used in all paints with Cu_2O as main toxin. In the first set, the content of Cu_2O ranged from 76.1 - 59.7% by weight based on dry paint film; in the second, 42.8 - 28.5%; and in the third, 38.5 - 18.9%. Members of the first set, which may be classified as contact-leaching, resisted fouling for a period not exceeding 13 continued months, while members of the third set, which may be categorized as soluble-matrix, were efficient for 4-7 months only. Members of the second set, named here as combined-mechanism type, exerted an intermediate efficiency between the contact-leaching and soluble-matrix types, yet were nearer to those of the first set. A longer protection period could not be obtained in this type of compositions.

The application of each class depends on many factors including economy, the physical and chemical properties of the encountered waters, and the desired frequency of recoating.

INTRODUCTION

Applied research in the field of anti-fouling (AF) coatings is challenging. An anti-fouling coating has to satisfy in a protective film two contradicting factors: it has to give away certain ingredients to kill or repel fouling larvae, which means consumption; and yet, it has to maintain cleanliness and physical integrity for long immersion periods, which means permanency.

In an environment where all conditions favor attack by fouling organisms¹ as well as physical and chemical erosion^{2,4} and rusting,⁵ the challenge of achieving effective durability becomes greater. This situation can only be met by intensive work in two vastly different directions. The first is to try to determine the mechanism of fouling attachment on submerged structures, the stages undergone by a macro-organism from pre-

liminary swimming form to adult adherent productive form, and the conditions which favor or retard the succession of development.^{6,9} The second is to acquire knowledge on the mechanism of function of anti-fouling films^{6,10,11} which requires thorough knowledge of the nature of the individual ingredients of the film, their interaction with each other and with the constituents of the environment, and how they are influenced by governing parameters⁴ in the surrounding nature.

In a team of specialists in marine ecology, hydrography, anti-corrosive and anti-fouling coatings, the field and laboratory investigations on the various disciplines can be integrated to ultimately solve problems of great technological importance in the protection of ship and submerged installations.

Selected background for the ecological side of the present work can be found in articles on the succession and settling behavior of fouling organisms in Alexandria harbor,¹ and the physical and chemical characteristics of Alexandria western harbor relevant to fouling and anti-fouling paints.^{2,4} Selected investigations of direct relevance to the present work are found in an article on the effect of rosin on the efficiency of anti-fouling paints,¹² and another on the role of plasticizer type and content in the long term efficiency of anti-fouling coatings.¹³

In the present work, which was performed prior to the last two investigations^{12,13} but not hitherto published, the value of employing high toxin content in cuprous oxide-based anti-fouling coatings for prolonging the protection period is demonstrated by tests in the laboratory, and in natural environment where severe fouling conditions cannot be matched probably anywhere else in the world.¹⁴

Until the present time, cuprous oxide dominates the field of toxins in commercial anti-fouling paints for reasons already well established, such as its widest toxic effect on the majority of fouling organisms, its moderate solubility in sea water (being neither too high nor too

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Presented by Dr. Ghanem at the Symposium of Marine and Anti-Fouling Paints at the American Chemical Society Meeting in Miami Beach, Fla., Sept. 10-15, 1978.

Table 1—Contact-Leaching Anti-fouling Compositions (Dry film)

Constituent	Composition						
	1	2	3	4	5	6	7
Vinyl copolymer	10.5	10.5	10.5	11.5	11.5	12.8	12.8
Plasticizer	3.2	3.2	3.2	3.5	3.5	3.9	3.9
Rosin	2.7	2.7	2.7	3.0	3.0	3.3	3.3
Rosin mod. phenolic resin	1.8	1.8	1.8	2.0	2.0	2.2	2.2
Cuprous oxide	76.1	67.9	59.7	74.4	66.4	72.4	64.6
Zinc oxide	1.3	1.8	2.3	1.3	1.8	1.3	1.6
Iron oxide red	2.7	10.4	18.1	2.6	10.1	2.4	9.9
China clay & additives	1.7	1.7	1.7	1.7	1.7	1.7	1.7
% Cu ₂ O by volume	42.8	37.8	31.3	40.1	33.4	37.2	34.5
Pigment volume conc.	47.3	47.8	47.9	44.5	42.4	41.2	39.0
Pigment/Binder ratio	4.5	4.5	4.5	4.0	4.0	3.5	3.5

low in comparison with other copper compounds), its being a good pigment which fulfills all the requirements of a good paint pigment, and its moderate cost in comparison with heavy toxic counterparts, such as mercury, tin, and silver.

However, the position of cuprous oxide in this field has been challenged in recent years by competitors which claim the same wide toxic coverage with much less environmental impact such as provided by organotin compounds¹⁵⁻¹⁷ and polymers,¹⁸⁻¹⁹ and purely organic toxic compounds which degrade to harmless products after being released in the sea.²⁰

Effective formulations containing both cuprous oxide and organotin compounds, and organotin compounds only, will be described in the next articles. Work on anti-fouling coatings which contain no toxic ingredients at all is in progress after some positive signals were obtained.²¹

METHODS

Materials used in this investigation are described in detail in the Appendix.

Testing the efficiency of the composition was performed in three manners:

(1) Accelerated testing in glycine, and after immersion in acid and alkali^{6,23} for determining in a short time whether or not the composition would be worthy of further testing, and whether or not the toxic element is released independent of the solubility of the matrix ingredient in sea water.

(2) Normal laboratory leaching rate experiments^{6,24} for determining the continued leaching of copper from the composition for long periods of immersion in sea water. The effective leaching rate of straight cuprous oxide formulations for fouling prevention was established at 10 $\mu\text{g}/\text{cm}^2\cdot\text{day}$.^{6,23} This limit acts as a second sieve for proposed and experimental formulations.

(3) Raft testing for determining, preultimately, both the physical durability and the anti-fouling efficiency of the coating in a natural environment. This simple submerging device was used prior to building the testing station in the fouling-rich Alexandria harbor.¹⁴

Ultimate testing should be carried out on represen-

tative areas on ship hulls; the ship should be of known schedule and the areas should be periodically examined.

RESULTS AND DISCUSSION

Three sets of formulations, each set representing a class of anti-fouling paints, were prepared and checked in the laboratory according to the conventional techniques employed in industrial research laboratories. Each set comprised compositions belonging, respectively, to the so-called contact-leaching, combined-mechanism, and soluble-matrix class. Hence, the distinctive feature in each set is the cuprous oxide content; the rest of the constituents were kept the same except where compositional factors call as shown in the following tables.

Contact-Leaching Compositions

This set of seven compositions is given in Table 1. It can be observed that a small amount of zinc oxide is always present. This small addition was meant for improving the paint film physical properties and not for its toxicity which is estimated at one-fifth that of Cu₂O. The pigmentation ratio was kept at three levels, namely, 4.5, 4, and 3.5 pigment to 1 binder by weight. The Cu₂O contents in the pigment mixtures used were 93, 83

Table 2—Amounts of Copper Leached Out From Contact-Leaching Anti-fouling Compositions in the Glycine and Acid-Alkali Tests

Composition	Cu ₂ O Content by Weight	Glycine Test mg Cu/cm ² 3 days	Leaching Rates $\mu\text{g}/\text{cm}^2\cdot\text{day}$	
			After Acid	After Alkali
1	76.1	4.22	19.46	27.35
2	67.9	4.22	18.41	22.62
3	59.7	3.87	21.57	18.41
4	74.4	4.57	19.98	25.25
5	66.4	4.92	14.20	21.57
6	72.4	4.80	19.46	18.93
7	64.6	4.60	16.31	22.09

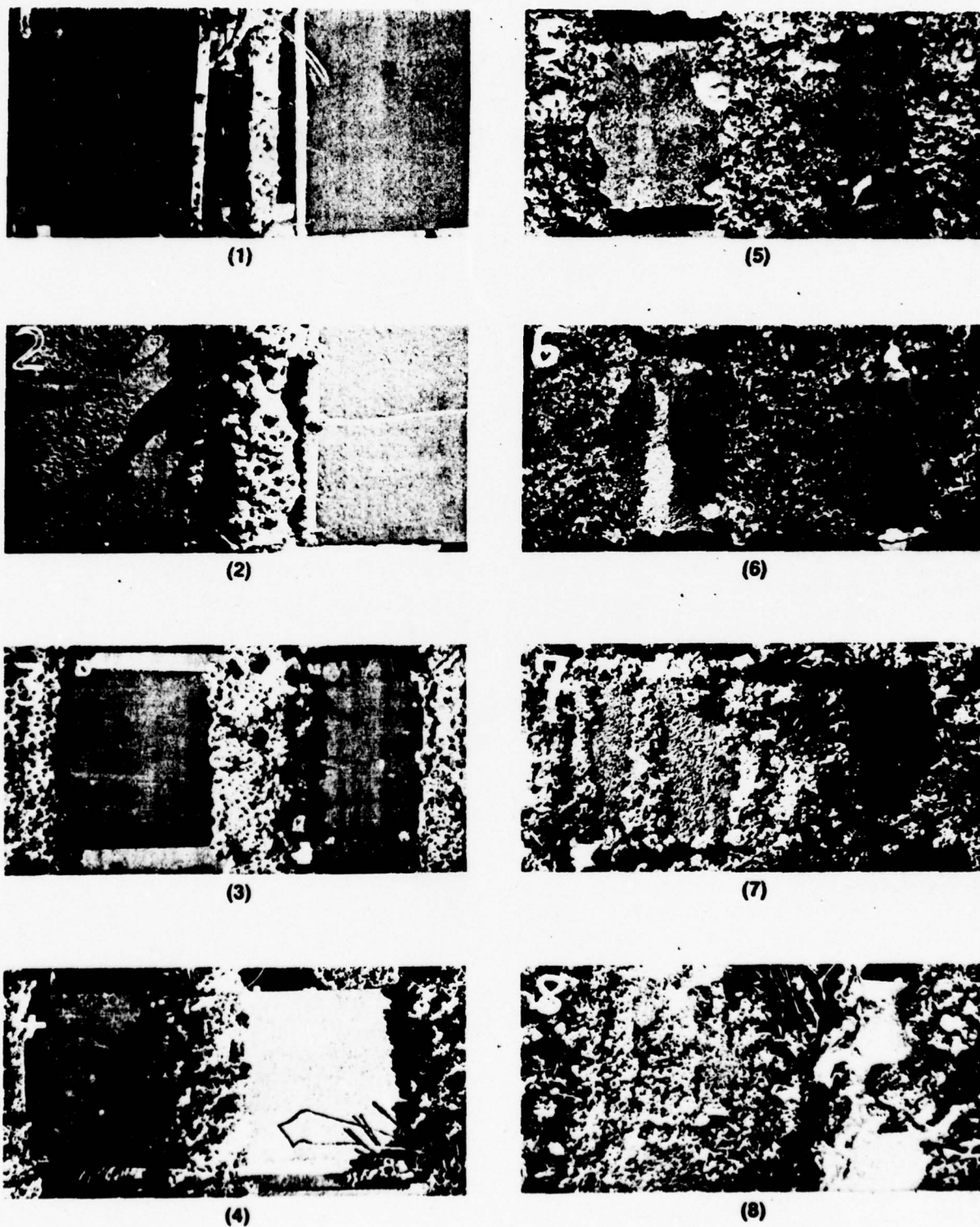


Figure 1(A)—Contact-type copper formulations. Behavior of Composition 2 during 362 days of immersion in the sea. Days Immersed: 1-30; 2-60; 3-91; 4-121; 5-212; 6-242; 7-333; and 8-362

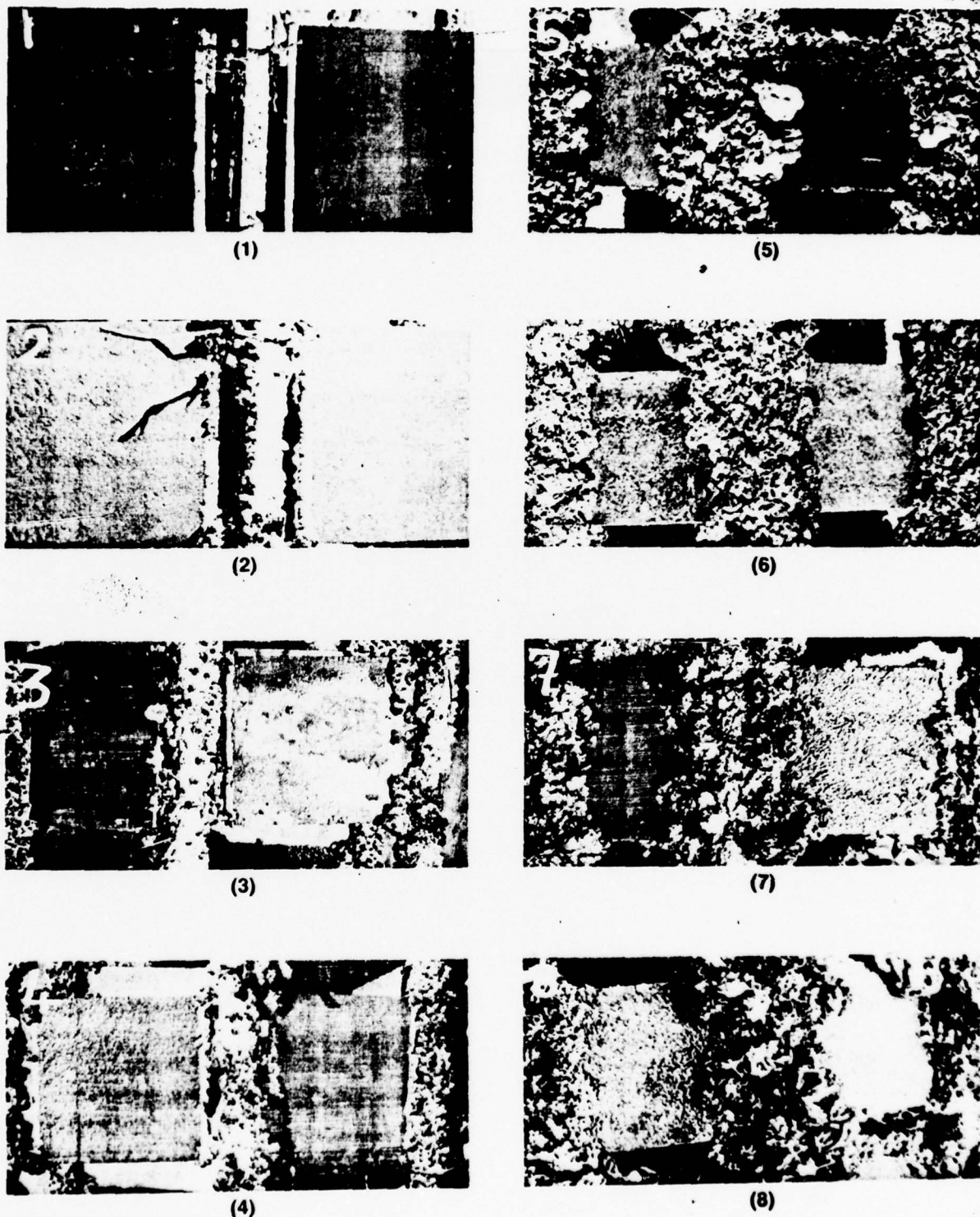


Figure 1(B)—Contact-type copper formulations. Behavior of Composition 7 during 362 days of immersion in the sea. Days immersed: same as Figure 1(A)

**Table 3—Normal Leaching Rates
Of Contact-Leaching Anti-fouling Compositions**

Composition	Leaching Rate $\mu\text{g}/\text{cm}^2\cdot\text{day}$			
	Initial	After 30 d.	After 60 d.	After 90 d.
1	77.7	50.7	31.6	26.3
2	74.3	31.6	30.5	32.6
3	64.2	13.2	23.7	26.3
4	60.8	28.4	25.2	29.5
5	87.9	26.3	21.0	21.0
6	91.2	19.0	26.3	19.0
7	81.1	31.6	28.4	24.2

and 73% by weight. Accordingly, the high Cu_2O content which distinguishes this class ranges from 76.1 - 56.8% by weight of dry film, which corresponds to 42.8 - 28.2% by volume of dry film. Replacement of a portion of cuprous oxide by fillers and extenders in the anti-fouling compositions was performed to test efficiency of less costly formulations. Finally, it can be observed that the pigment volume concentration (PVC) is generally higher than that customarily found in normal anti-corrosive and conventional coatings. This is natural in AF compositions depending on leaching out toxic particles leaving channels for further leaching from a strong and inert binder.

The results of the accelerated tests of anti-fouling compositions 1 to 7 are given in Table 2. The glycine test gave values ranging from 3.87 to 4.92 $\text{mg}/\text{cm}^2\cdot 3$ days, which are well above the optimum level of 1.3 - 2.5 put forward by many investigators.^{6,23} The acid-alkali test gave values well above the optimum level of 10 $\mu\text{g}/\text{cm}^2\cdot\text{day}$.

At this stage normal copper leaching rates should be determined for the desired period of protection. The data given in Table 3 should therefore be considered indicative of efficiency as tests were followed for three months only. It is shown that the leaching rates of all compositions are well above the optimum of 10 $\mu\text{g}/\text{cm}^2\cdot\text{day}$ with a trend of continued above-optimum leaching for several months further.

Coupled with physical and rheological properties of both paint and coating for all compositions, the leaching experiments recommended them for environmental testing.

Figure 1 shows photographs of the behavior of anti-fouling compositions 1-7 during a raft testing period of one year starting May 4 and ending April 30. After one month of immersion a very thin gelatinous film of slime composed of bacteria and diatoms may be observed in the pictures. It was reported⁶ that such slime film contains considerable amounts of organic and inorganic detritus materials. This was the only type of settlement on this set of compositions. The slime film became thicker at the beginning of the third month and continued until the end of the immersion period. It was claimed⁶ that a slime film may accumulate large quantities of the poisons leached out from the coating and may contain as much as a thousand times the toxic

concentration found in a saturated sea water solution. The slime film might have improved the performance of the compositions by keeping relatively high concentrations of copper at the surface or might have increased the leaching rate because of the matrix attack. In view of the high cuprous oxide content in this set of compositions, the slime film might have acted as a store for copper in the form of simple ionic or insoluble form of basic copper carbonate and copper oxychloride which contributed in keeping the painted panels clean during the one year of immersion.

However, it must be noted that any mechanical damage to the coated panels during lifting for photographic recording would provide a suitable spot for larval attachment. This is clearly shown on the panel carrying composition 2 where growth took place irrespective of the toxic edges which indicates that the range of protection of released copper is limited to the close vicinity of the surface. Furthermore, it was impossible to avoid creeping of intensive fouling created at the ribs of the supporting frames and the pores and sharp edges of the plates towards the interior of the plates. A new design of supporting the plates to minimize fouling creeping emerged^{13,27} and was used in later experiments.

Combined-Mechanism Compositions

The three compositions shown in Table 4 are characterized by an intermediate cuprous oxide content, namely, 42.8, 35.6, and 28.5% by weight. To help disintegration of the matrix for sufficient copper release, a high content of rosin amounting to about 30% by weight of the total binder is incorporated. A small content of a rosin-modified phenolic resin compensates, with its higher molecular weight and lower acidity, for the gradual reduction in film integrity caused by rosin. In all three compositions the total pigment content is 71.74% by weight of dry film; the difference between the total pigment and the cuprous oxide is covered by pigments of similar specific gravities. Thus, a gradual decrease of the cuprous oxide weight and volume percent is maintained from composition 8 to 10. The pigment/binder

**Table 4—Combined-Mechanism Anti-fouling Compositions
(Dry film)**

Constituent	Composition		
	8	9	10
Rosin WW	8.8	8.8	8.8
Vinyl copolymer	14.7	14.7	14.7
Plasticizer	2.6	2.6	2.6
Rosin mod.			
phenolic resin	2.5	2.5	2.5
Cuprous oxide	42.8	35.6	28.5
Zinc oxide	4.3	4.3	4.3
Iron Oxide	3.4	10.6	17.7
Barytes	16.3	16.3	16.3
China clay & additives	4.6	4.6	4.6
% Cu_2O by volume	20.2	15.1	13.2
Pigment vol. conc	35.3	35.7	36.0
Pigment/Binder ratio	2.5	2.5	2.5

Table 5—Amounts of Copper Leached out From Combined-Mechanism Compositions in the Glycine Test

Composition	Cu ₂ O Content by Weight	mg Cu/cm ² ·3 days
8	42.80	3.43
9	35.60	3.20
10	28.50	3.00

ratio in the three compositions is down to about 2.5:1 by weight.

The results of the glycine accelerated test are given in Table 5. It is shown that copper is released in amounts above the acceptable limits and is proportional to the cuprous oxide content in the film thus entitling the compositions for further testing.

A photographic record of fouling resistance of these compositions is shown in Figure 2. Except for a few localized fouled areas attributed to mechanical damage of the panels during lifting and reimmersion for photographic recording, all three compositions showed good anti-fouling properties for a period of about 10 months; at the end of one year the panels were completely fouled and looked like blanks with only small unfouled areas.

Soluble-Matrix Compositions

The compositions belonging to this class are given in Table 6. The mechanism of release depends on the gradual dissolution of certain constituents of the binder mixture in sea water thus exposing fresh toxin. In spite of its brittleness and low film properties, rosin is so far the most widely used cobinder to provide the desired sacrifice; it is employed in these compositions in about 46% by weight of the total binders. The vinyl copolymer compensates for the lost stability, and ester gum and an alkyd resin enhance the required elasticity.

The content of cuprous oxide ranges from 38.5 to 18.9% by weight of the dry film. An overlap may seem to occur between the compositions of the previous class and certain compositions in this class (compositions 10, 11, 12, 13, and 15), but the total pigment to binder ratios in the present class are much lower, being 1.8-0.9:1.

The results of glycine and acid-alkali accelerated tests are given in Table 7. From the glycine test it is possible to exclude directly compositions 16 and 18-20 from further testing as their leaching rates are 0.63 mg Cu/cm²·3 days and lower, which are well below a limit of 0.9 mg/cm²·3 days put forward by other investigators. All these compositions belong to a pigmentation ratio of 0.9 to 1.2:1 (or a pigment volume concentration of 15.8-20).

All leaching rates after alkali extraction were quite acceptable, being well above the optimum rate of 10 µg/cm²·day. This was not surprising since a good part of the matrix is rosin which would have dissolved in the alkali exposing Cu₂O to sea water. After acid extraction, all compositions gave values very near the margin of efficiency which indicates that after removal of copper from its surface, the compositions release Cu₂O at a



(A)



(B)



(C)



(D)

Figure 2—Combined mechanism formulations. Behavior of Compositions 8, 9, and 10 during 239 days of immersion in the sea. Days immersed: A-60; B-90; C-182; and D-239

Table 6—Soluble-Matrix Anti-fouling Compositions (Dry film)

Constituent	Composition									
	11	12	13	14	15	16	17	18	19	20
Rosin WW	16.9	16.9	18.0	18.0	18.0	20.4	20.4	23.7	23.7	23.7
Ester gum	6.1	6.1	6.8	6.8	6.8	7.7	7.7	8.9	8.9	8.9
Alkyd resin	7.1	7.1	8.0	8.0	8.0	9.1	9.1	10.5	10.5	10.5
Vinyl copolymer	5.6	5.6	7.2	7.2	7.2	8.2	8.2	10.5	10.5	10.5
Cuprous oxide	38.5	32.2	36.0	30.0	24.0	32.7	27.3	28.4	23.7	18.9
Zinc oxide	3.8	4.0	8.0	8.0	12.0	2.9	5.0	6.3	7.0	9.5
Iron oxide	12.5	10.5	14.6	12.5	14.5	9.5	4.5	11.5	7.2	9.5
Barytes	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4
China clay & additives	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
% Cu ₂ O BY VOLUME	14.5	12.5	12.3	10.5	8.4	10.6	9.2	8.1	6.9	5.5
PIGMENT VOL. CONC.	26.9	24.5	26.0	23.7	24.0	20.0	17.5	17.5	15.7	15.8
PIGMENT/BINDER RATIO	1.8	1.8	1.5	1.5	1.5	1.2	1.2	0.9	0.9	0.9

rate governed by the relative contents of rosin to cuprous oxide. For example, where the ratio of rosin to copper was too low, as in compositions 11 and 13 to 15, the leaching rate after acid extraction was also relatively low. On the other hand, too high a rosin ratio would not produce the desired long term efficacy for its objectionable effect on pot stability, film properties, and its enhanced dissolution in warm waters.

Photographic recordings of raft exposure are given in Figures 3 and 4. Although this test started in September, the condition of the blanks indicates intensive fouling activity. Water temperature of 27°C was recorded on October 27. The temperature went below 20°C only after the first half of December.

The formation of slime was general on all the plates from the early weeks of immersion and became thicker with time. In contrast to slime formed on contact-leaching compositions, this slime does not seem to accumulate toxic concentrations high enough to repel fouling larvae; settlement of individuals of serious fouling organisms like barnacles and tube worms was observed on some plates in the early months.

From the condition of the plates along the immersion period, one could classify this set of compositions in two groups; the first group comprises compositions 11

to 15 which have pigment/binder ratios of 1.8:1 and 1.5:1. These compositions are characterized by lower slime film formation and longer anti-fouling capacity than the rest of the compositions. If fouling initiated at mechanically damaged areas is neglected, the overall protection period can be estimated at not more than eight months. The second group comprises compositions 16 to 20 which have pigment/binder ratios of 1.2:1 and 0.9:1. It is clear from the pictures that these compositions are hardly suitable for temperate fouling-rich waters. As soon as surface copper is removed, the normal leaching rate of these compositions is too low to protect from attachment and growth of fouling organisms; protection lasted three months only.

CONCLUSIONS

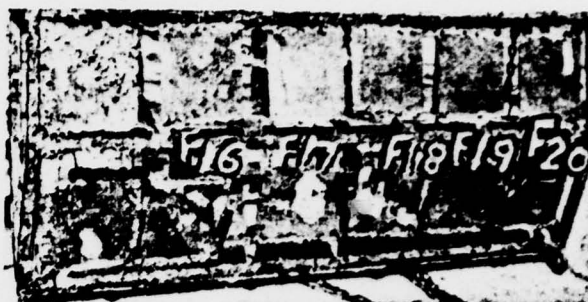
There seems to be an upper limit of the period for fouling prevention by coatings mainly depending for their toxicity on cuprous oxide. The curve in Figure 5 is drawn from most of the compositions prepared and tested as described above, where the insoluble binder is a vinyl copolymer and the soluble one is mainly rosin; it shows that the maximum protection period likely to be

Table 7—Soluble-Matrix Anti-fouling Compositions; Amounts of Copper Leached in Glycine Solution And Sea Water after Acid and Alkali Extractions

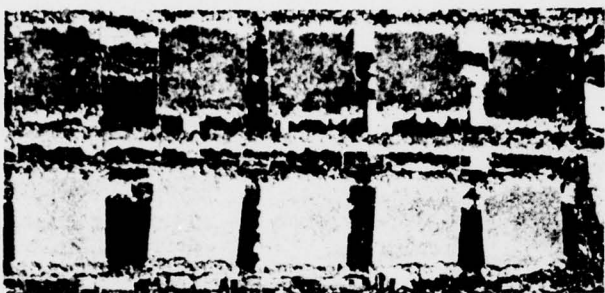
Composition	Cu ₂ O Content by Weight	mg Cu/cm ² ·3 days In Glycine Solution	Leaching Rates μg Cu/cm ² ·day	
			After Acid	After Alkali
11	38.5	0.99	8.94	27.3
12	32.2	1.65	9.99	21.0
13	36.0	1.20	9.90	12.1
14	30.0	1.40	9.90	20.5
15	24.0	1.20	8.42	21.0
16	32.7	0.63	9.99	18.9
17	27.3	1.10	11.05	22.6
18	28.4	0.55	9.99	20.5
19	23.7	0.51	9.49	18.4
20	18.9	0.35	9.99	20.5



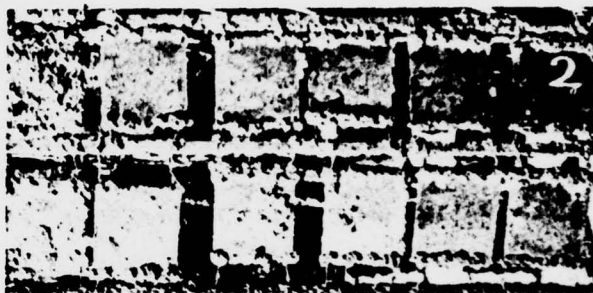
(A)



(A)



(B)



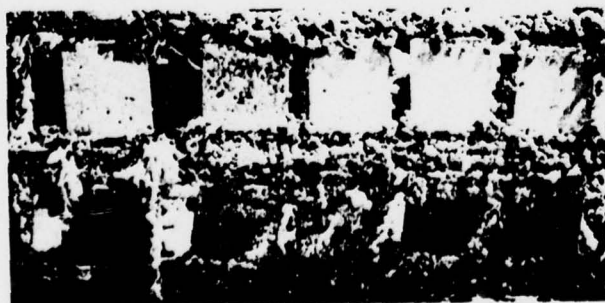
(B)



(C)



(C)



(D)

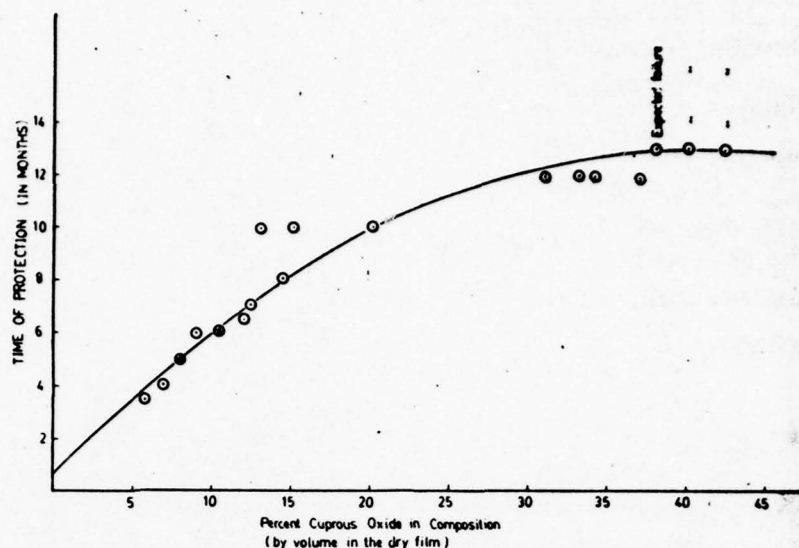


(D)

Figure 3—Soluble-matrix formulations. Behavior of Compositions 11 to 15 during 239 days of immersion in the sea. Days immersed: same as Figure 2

Figure 4—Soluble-matrix formulations of low-pigment-binder ratio. Behavior of Compositions 16 to 20 during 239 days of immersion in the sea. Days immersed: same as Figure 2

Figure 5—Relationship between the period of protection in natural environment in months and cuprous oxide % in the composition by volume



achieved by such compositions in temperate, fouling-rich waters is 13 months.

For extended periods of protection, research should be directed to areas where other binder systems are used or, higher efficiency toxics may supplement or replace cuprous oxide. These and other non-toxic trends are being investigated.

ACKNOWLEDGMENT

This work was performed prior to and during research contract N00014-75-C-1112 between the National Research Centre of Egypt and the Office of Naval Research of the Department of the United States Navy.

We are also grateful to BASF, AG Ludwigshafen, for supply of starting materials of their own and other companies' products, and for many fruitful discussions with Dr. Neubert, Dr. Brüssmann, and Dr. Morcos of AWETA (Applied Research Dept.), of BASF, AG.

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APPENDIX

MATERIALS

RESINS:

Vinyl Copolymer: Laroflex MP 35, previously known as Vinoflex MP400, was obtained from BASF, West Germany. It is a non-hydrolyzable, internally plasticized film-former derived from vinyl chloride and vinyl isobutyl ether. It is readily soluble in a large number of solvents yielding high-bodied paints with comparatively low viscosity. It is also compatible with a wide range of resins.

External Plasticizer: Lutonal M 40. It is a medium viscosity polyvinyl methyl ether also obtained from BASF. It is used as a plasticizing agent for Laroflex MP 35. Polyvinyl ethers are generally light-stable, non-hydrolyzable plasticizing resins. Lutonal M 40 is soluble in water but in the presence of vinyl copolymers its solubility is much reduced and would impart controlled swellability to the composition which turns to a reservoir for copper-sea-water-constituents reaction products.^{13,22}

Rosin Modified Phenolic Resin: Ennesin G.H. 103. It is a product of Leon Frenkel Ltd., England. Glycerol is the esterifying alcohol. Its acid value (in mg KOH/g) is 5-10; its specific gravity is 1.12.

Alkyd Resin: Ennelkyd 609/75 is a long oil pentaerithritol alkyd resin obtained from Leon Frenkel Ltd., England. The modifying alcohol is segregated marine oil, its acid value (in mgKOH/g) is 5-10; its specific gravity is 1.05.

Rosin WW: A quantity was obtained from the import/export General Company for Trading and Chemicals, Cairo, Egypt.

TOXIC AND NONTXIC PIGMENTS:

Cuprous Oxide: A micronized, highly dispersable quality Cu_2O was obtained from Nordox A.S., Bryn, Norway. In this fine form, 95% of the material has a particular size under 4 microns. Its total copper is approximately 86%; Cu_2O about 96%; free copper maximum 0.5%; and a specific gravity of about 6.

Iron Oxide Red: A product imported from China by the General Co. for Trading and Chemicals, Cairo, Egypt. It is of a micronized grade, specific gravity 5.10.

Zinc Oxide: Pure, chemical reagent was obtained from Veb Laborchemie, Apolda, East Germany.

China Clay: 35 BMM grade. It was obtained from the English China Clays Co. Ltd., the specific gravity is 2.6.

Baryte: A micronized grade, imported from China; its specific gravity is 4.49.

SOLVENTS, THINNERS AND DILUENTS:

Were of the grades conventionally used in the industry. Blends composed of ethylene glycol monoethyl ether acetate, white spirit, xylene and butyl acetate were suitable for all compositions.

DOCUMENT

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Some Studies on Aluminium Paints.

Paint Manufacture, 34, November 1977

By

M.A. Abou-Khalil and N.A. Ghanem

Some Studies on Aluminium Paints

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Thirty-nine formulations, based on aluminium, were prepared in the laboratory. These formulations could be classified into three groups. The aim of this classification is to study the effects of type of binder, inhibitive pigments and inert pigments on the efficiency of the aluminium paints. The prepared paints were first tested in the laboratory and then in a raft testing station in the eastern harbour of Alexandria, for a period of six months.

It has been found that all the formulations passed the actual exposure test. The formulations which were based on chlorinated rubber or a blend of vinyl copolymer binder showed more corrosion prevention than the other formulations. The incorporation of some inhibitive pigments into the aluminium paints improved their efficiency. Also the addition of china clay or talc has improved the efficiency of the aluminium paints.

Since the corrosion of iron or steel is an electrochemical reaction in nature, it follows that in order to inhibit corrosion it is necessary to stop the flow of current by suppressing either the cathodic or the anodic reaction, or by inserting a high resistance in the electrolytic path of the corrosion current. The three methods of suppression are called cathodic, anodic and resistance inhibition respectively.

In previous publications^(1, 2, 3), the paints which suppress the anodic reaction were concerned. Interference with the cathode reaction is more difficult because paint films are normally so permeable to water and oxygen as to permit the cathodic reaction to proceed unhindered⁽⁴⁾.

In this work, the aim is to throw more light upon the resistance inhibition paints. The protection action of this class depends on the formation of an impermeable film to act as a physical barrier between the substrate and the surrounding medium⁽⁵⁾. The presence of metallic aluminium as a sole pigment is the main characteristic of this group of paints. It has been suggested⁽⁶⁾ that the main function of

the aluminium flake pigment, arising from its orientation in the plane of the paint film, is to lengthen the path of moisture as it seeks to permeate the paint coating. Aluminium has good reflectance in the visible, infrared and ultraviolet. Hence it can protect the binder from these rays⁽⁷⁾.

Materials and methods

Materials

Pigments

- 1— Aluminium paste (65 per cent): Was obtained as a 2kg sample from the General Company for Trading and Chemicals, Cairo.
- 2— Talc: Obtained from the previous company.
- 3— Iron oxide (130F): Was obtained from Bayer, Leverkusen, Germany. Its pH is 5.5.
- 4— Barytes: Was obtained from the General Company for Trading and Chemicals, Cairo.
- 5— China clay: Obtained from English China Clays, Company, Ltd, England.
- 6— Titanium dioxide: Was obtained from the General Company for Trading and Chemicals, Cairo.
- 7— Micaceous iron oxide: Was obtained from Bayer, Germany.

Binders

- 8— Epoxy resin: Obtained as two components from Ciba Geigy, Germany.
- 9— Vinyl copolymer: Laroflex MP 35 was obtained from BASF, Germany.
- 10— Phenolic resin: Wreinyl 265 (R552) was obtained from Resinous Chemicals Ltd, England.
- 11— Rosin-modified phenolic resin: Wresinite 1 (R201) was obtained from the previous company.
- 12— Chlorinated rubber: Was obtained from ICI, England.
- 13— Coumarone-indene resin: Was obtained from R. H. Cole, Ltd, England.

Plasticizers

- 14— Chlorinated paraffin N50: Was obtained from Hoechst AG, Germany.

Inhibitive Pigments

- 15— Basic lead carbonate: Was obtained from Associated Lead Manufacturers, Ltd, England.
- 16— Basic lead sulphate: Was obtained from the previous company.
- 17— Calcium plumbate: Was obtained from Associated Lead Manufacturers, Ltd, England under the name Caldio.
- 18— Basic lead silicochromate: Was obtained from National Lead Company, USA.
- 19— Zinc phosphate: It was obtained from Imperial Smelting Corporation Ltd, England.
- 20— Barium metaborate: It is a product called Busan 11-M1 of Buckman Laboratories, Inc, USA.

Methods

Preparation of the paint

The vehicle was dissolved in suitable solvents. The pigment mixture was first mixed with the vehicle solution to produce a semi-paste. The pigment was dispersed in the vehicle solution using a ball mill. After the paint has been ground, the aluminium paste was incorporated to produce the ready-mixed paint.

Laboratory corrosion resistance⁽⁸⁾

Mild steel panels (5 x 10cm) were degreased using suitable solvents and then sandpapered. The panels were painted with the prepared paints and left to dry for seven days. They were edged with wax to prevent attack from the edges, and one face of each panel was scratched with a sharp blade to expose the bare metal. The panels were then exposed to synthetic sea water for up to 670 hours. At the end of this time they were washed with distilled water and dried. The amount of rust on each panel was observed. The adhesion along the groove was determined by the normal method.

Preparation of steel plates for testing in natural environment⁽⁹⁾

Mild steel plates (20 x 35cm) were used. Any rust present was removed by sandpapering the plates. The plates were cleaned with a cloth wet with pure solvents to remove any film of oil

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The plates were allowed to dry solvents have evaporated at temperature. They were rubbed with a clean lintless cloth to any adherent dirt.

Exposure test (10)

The test includes the exposure of painted plates to the actual conditions. The previously used plates were painted first by coats of the aluminium paint and by one coat of the antifouling solution. The antifouling composition was already proved to be successful (see Table (1)). The stands for supporting the plates were erected and the steel plates were hanging from the top frame by joints in order to prevent the risk of fouling onto the next. Figures 1 and 2 show the old and the improved stand. The exposure was carried out in a floating station in the harbour water of Alexandria. A detailed description for this station is given in a previous publication (11). Inspection was carried out monthly during the period of the test. The duration of the test was six months.

Experimental results and conclusions

Forty-nine formulations, based on aluminium, were laboratory prepared. In the previous publication (3), the factors influencing the formulations of the anti-fouling paints were concerned. The formulations could be classified into three main groups. In the first group a series of paints was prepared by the effect of binder on the efficiency of the aluminium paints. The effect of incorporating of some inhibitive pigments into the aluminium paint was concerned in the second group. The aim of the third group is to study the effect of using different types of inhibitive pigments on the behaviour of aluminium paints.

Group No 1

This group of paints comprises twenty-seven formulations as can be seen from table 2. Six different types of binder were used in order to study the effect on the efficiency of the aluminium paints. The aluminium content ranged from 10 to 50 per cent by weight of the total paint film.

These prepared paints were first tested in the laboratory and then in a floating station in the eastern harbour of Alexandria. Table 2 summarises the laboratory tests data.

In order to expose these paints to sea water test, they should be coated by a layer of antifouling paint. The antifouling paint used was already proved to be successful. It has been found that the formulations based on phenolic resins were not compatible

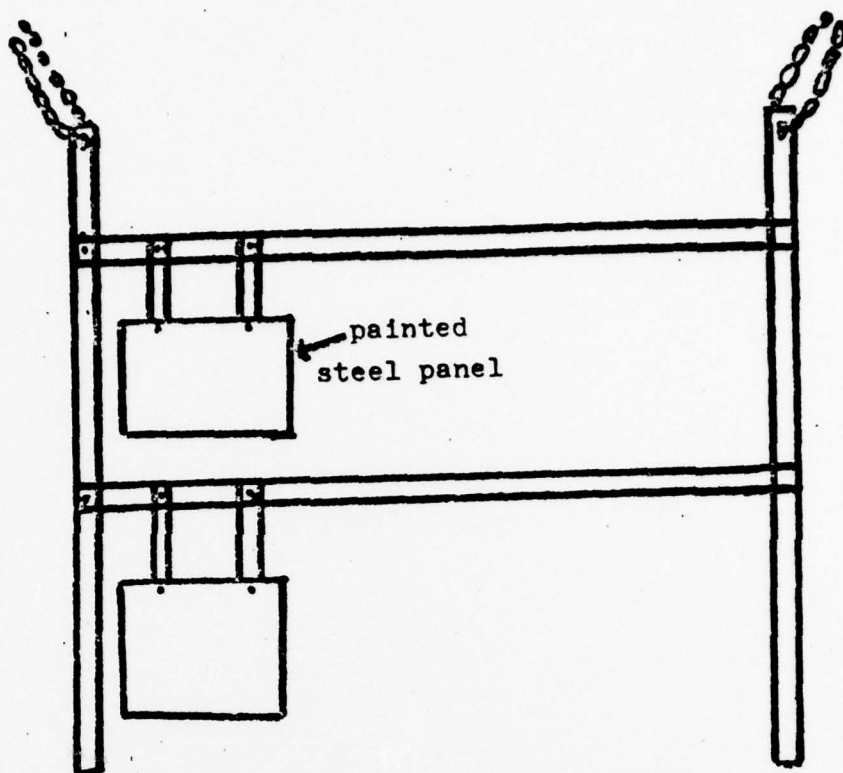


Fig. (1) The improved stand with the painted steel panels suspended from it.

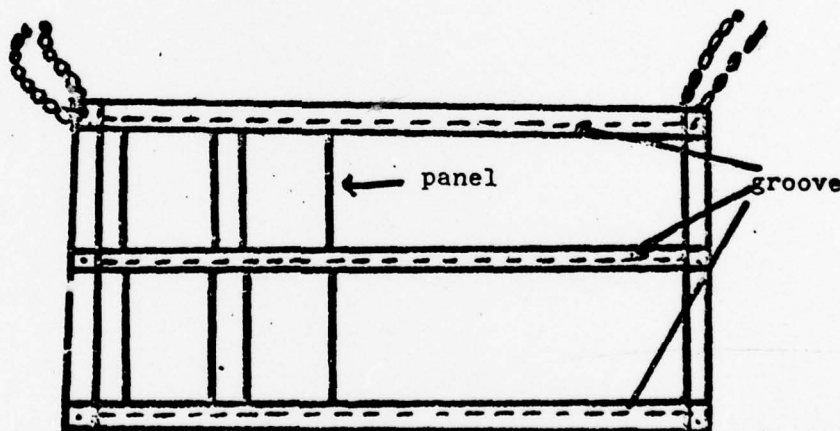


Fig. (2) The old stand in which the panels were supported through a groove.

with the antifouling top coat. These phenolic-based formulations were excluded from being exposed in the sea water and only twenty-two formulations were tested in raft testing station in the eastern harbour of Alexandria. All the paints of this group passed this test which has been continued for a period of six months.

Paints Group No II

Six formulations were prepared in order to study the effect of incorporating some inhibitive pigments into the aluminium paints. Six different types of inhibitive pigments were used for this purpose. These pigments were: 1 Basic lead carbonate; 2 Basic lead sulphate; 3 Calcium plumbate; 4 Basic lead silicochromate; 5 Zinc phosphate; 6 Barium metaborate.

The aluminium content was 30 per

cent by weight of the total paint film and the inhibitive content was 15 per cent by weight of the total paint film. All the formulations contained a blend of vinyl copolymer, rosin-phenolic and phenolic resin in the ratio of 5:2:3 of the total binder (see Table (4)).

The laboratory corrosion test of these formulations, as shown in Table 5, indicates that all the paints of this group, except those with basic lead carbonate and barium metaborate, gave good prevention against the spreading of rust. It is clear that the incorporation of inhibitive pigments improved the efficiency of the aluminium paints and prevented rust from being extended along the exposed area.

On testing these formulations in a raft, they showed good corrosion

prevention during the course of the test (six months).

Paints Group No III

One of the interesting things is to study the effect of incorporating some inert pigments into the aluminium paints and to see how the efficiency of the paints will be affected. Six different inert pigments were used in this study. Table 6 summarises the paint film compositions of these formulations.

On testing these paints in the laboratory (see Table 7), it has been found that the formulations with talc and china clay gave better corrosion prevention than the other formulations.

All these formulations passed the raft test which had been continued for a period of six months.

Conclusions

- 1 All the laboratory prepared aluminium paints have passed the actual exposure test (six months).
- 2 Aluminium paints formulated with chlorinated rubber or with a blend of vinyl copolymer and coumarone-indene resin, showed good corrosion prevention when they were tested in the laboratory.
- 3 The efficiency of the aluminium paints was improved by incorporating inhibitive pigments.
- 4 The incorporation of china clay or talc into the aluminium paints improved their efficiency.

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Table 1. Antifouling paint film composition

Composition	%
Cuprous oxide	75
Iron oxide	—
Talc	3
Vinyl copolymer	16
Plasticiser	1.5
Rosin-phenolic resin	3.0
Rosin	1.5
Total binder	22
Pigment: Binder	3.5

Table 2. Paint film compositions of Paints Group No I

Paint no	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Aluminium	50	40	30	20	10	50	40	30	20	10	50	40	30	20	10
Talc	—	10	20	30	40	—	10	20	30	40	—	10	20	30	40
Total pigment	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Epoxy binder	50	50	50	50	50	—	—	—	—	—	—	—	—	—	—
Vinyl copolymer	—	—	—	—	—	45	45	45	45	45	—	—	—	—	—
Plasticisers	—	—	—	—	—	5	5	5	5	5	—	—	—	—	—
Phenolic resin	—	—	—	—	—	—	—	—	—	—	45	45	45	45	45
Rosin-phenolic resin	—	—	—	—	—	—	—	—	—	—	5	5	5	5	5
Total binder	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Pigment : Binder	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Paint no	16	17	18	19	20	21	22	23	24	25	26	27			
Aluminium	50	40	50	40	30	20	10	50	40	30	20	10			
Talc	—	10	—	10	20	30	40	—	10	20	30	40			
Chlorinated rubber	37	37	—	—	—	—	—	—	—	—	—	—			
Plasticisers	13	13	—	—	—	—	—	—	—	—	—	—			
Vinyl copolymer	—	—	22	22	22	22	22	—	—	—	—	—			
Plasticisers	—	—	3	3	3	3	3	—	—	—	—	—			
Coumarone-indene	—	—	25	25	25	25	25	—	—	—	—	—			
Vinyl copolymer	—	—	—	—	—	—	—	22	22	22	22	22			
Plasticisers	—	—	—	—	—	—	—	3	3	3	3	3			
Phenolic resin	—	—	—	—	—	—	—	15	15	15	15	15			
Rosin-phenolic	—	—	—	—	—	—	—	10	10	10	10	10			
Pigment : binder	1	1	1	1	1	1	1	1	1	1	1	1			
Solvents mixture: A blend of xylènes, ethyl acetate and white spirit.															

Solvents mixture: A blend of xylenes, ethyl acetate and white spirit.

Table 3. Laboratory corrosion test data of Paints Group No I

Aluminium %	50	40	30	20	10
Epoxy binder	Rusting in the groove with spreading along it. Blistering in the paint film.				
Vinyl copolymer binder	Rusting in groove. Blistering.	Rusting in the groove only. No blistering.			
Phenolic Rosin-phenolic Binder	Rusting in the groove only. No blistering.				Rusting in the groove. Blistering.
Chlorinated Rubber binder	Light rusting in the groove only. No blistering.	—	—	—	—
Vinyl copolymer Coumarone-indene binder	Light rusting in the groove only. No blistering.				
Vinyl copolymer Phenolic Rosin-phenolic	Rusting in the groove. Loss in adhesion along the groove.				

Table 4. Paint film compositions of Paints Group No II

Paints No	28	29	30	31	32	33
Aluminium paste	30	30	30	30	30	30
Talc	5	5	5	5	5	5
Basic lead carbonate	15	—	—	—	—	—
Basic lead sulphate	—	15	—	—	—	—
Calcium plumbate	—	—	15	—	—	—
Basic lead silicochromate	—	—	—	15	—	—
Zinc phosphate	—	—	—	—	15	—
Barium metaborate	—	—	—	—	—	15
Total pigment	50	50	50	50	50	50
Vinyl copolymer	22	22	22	22	22	22
Plasticisers	3	3	3	3	3	3
Phenolic resin	15	15	15	15	15	15
Rosin-phenolic resin	10	10	10	10	10	10
Total binder	50	50	50	50	50	50
Pigment : Binder	1	1	1	1	1	1

Solvents mixture: A blend of xylenes, ethyl acetate and white spirit.

Table 5. Laboratory corrosion test data of Paints Group No II

Type of inhibitive pigment	Laboratory corrosion test
Basic lead carbonate	Rusting in the groove only. Light blistering.
Basic lead sulphate	Rusting in the groove only. No blistering.
Calcium plumbate	Rusting in the groove only. No blistering.
Basic lead silicochromate	Rusting in the groove only. No blistering.
Zinc phosphate	Rusting in the groove only. No blistering.
Barium metaborate	Rusting in the groove only. Blistering.

Table 6. Paint film compositions of Paints Group No III

Paints No	34	35	36	37	38	39
Aluminium	30	30	30	30	30	30
Titanium dioxide	20	—	—	—	—	—
Talc	—	20	—	—	—	—
China clay	—	—	20	—	—	—
Barytes	—	—	—	20	—	—
Iron oxide	—	—	—	—	20	—
Micaceous iron oxide	—	—	—	—	—	20
Total pigment	50	50	50	50	50	50
Vinyl copolymer	22	22	22	22	22	22
Plasticisers	3	3	3	3	3	3
Phenolic resin	15	15	15	15	15	15
Rosin-phenolic resin	10	10	10	10	10	10
Total binder	50	50	50	50	50	50
Pigment : Binder	1	1	1	1	1	1

Solvents mixture: A blend of xylenes, ethyl acetate and white spirit.

Table 7. Laboratory corrosion test data of Paints Group No III

Type of inert pigment	Laboratory corrosion test
Titanium dioxide	Rusting in the groove. Blistering in the paint film.
Talc	Rusting in the groove. No blistering.
China clay	Rusting in the groove. No blistering.
Barytes	Rusting in the groove. Blistering in the paint film.
Iron oxide	Rusting in the groove only. Blistering in the paint film.
Micaceous iron oxide	Rusting in the groove. Blistering in the paint film.

Paint and Coating Industry in N America — Prospects and Problems

continued from page 18

Ireland have shown that a similar situation may exist there, with air masses passing over Northern Germany, Belgium and Holland eventually causing high ozone levels over Great Britain. If these reports are an accurate representation... the various European nations will also have to re-examine their pollution control strategies."

Meanwhile in California, the California Air Resources Board (CARB) is rapidly moving toward the development of new air pollution regulations for coatings being manufactured or marketed in the State. The Board's first priority is to develop regulations to require architectural coatings to be converted to low solvent systems, ie waterborne or high solids. CARB intends to exempt only those architectural coatings for which it can be demonstrated that no adequate low solvent substitutes are available.

The definition of architectural coating covers almost all trade sales, industrial and commercial maintenance coatings including such paints as traffic paints and high performance architectural coatings. It excludes marine, aircraft and automotive refinish coatings and does not cover factory-applied industrial coatings.

NPCA and the industry in California are actively engaged in discussions with CARB and the latest report indicates some softening of the approach in that priorities have been suggested which would provide more time for compliance for certain products. However, the issue has not yet been resolved.

The very stringent regulations proposed last year in Quebec may well be a harbinger of what can be expected in Canada at some time in the future. It would be useful for the industry in Europe to keep an eye on developments in the United States as well,

This article is based on a paper presented at the annual conference of the Paint-makers Association and is published by permission of the Association.

DOCUMENT

(6)

A Testing Station for Above-Water Paints.

Pigment and Resin Technology, 9, April 1978.

By

S.M. El-Saawy, M.A. Abou-Khalil and N.A. Ghanem

A testing station for above-water paints

By S. M. El-Saawy, M. A. Abou-Khalil* and N. A. Ghanem, Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt.

Summary

The present work describes a testing station for above-water paints in Egypt. The station has been constructed on Alexandria Seashore.

Introduction

The ultimate aim of our work is to evolve the best marine paint system suitable for our local marine conditions.[†] It is required to test the paints first in the laboratory and then in the actual environment.

Marine paints comprise underwater (anti-fouling and anticorrosive) and above water (anti-corrosive) compositions. To test the underwater paints a special floating station was built for this purpose; its description is given in a recent paper¹.

In the present work, a complete description of a new exposure testing station, for above water paints, is given. There is a tendency to carry out natural exposure tests in a severe condition and for this reason, Alexandria Eastern Harbour would seem to be ideal, because of the intensity of the sun light.

[†]See paper by the authors, March issue p5, "Anti-corrosion Behaviour of Some Laboratory Prepared Barium Metaborate-based Paints".

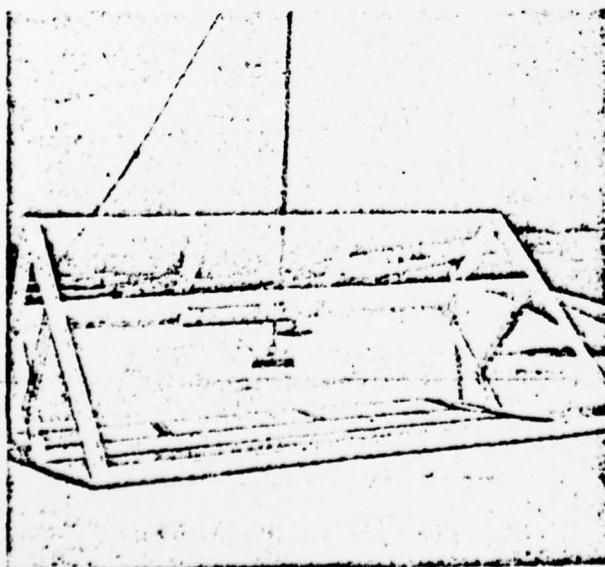


Fig 1. Above water testing station.

A description of the station

The design of the testing station was carried out by the authors. It is composed of steel bars fastened by bolts and having a rhomboid shape. Its dimensions are:

- 3.00 metres length,
- 1.80 metres width, and
- 1.50 metres height.

Two photographs of the station are shown in Figs 1 and 2.

Angle of Exposure:

The station was fixed in order to make an

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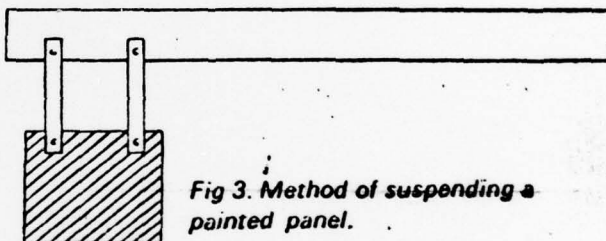


Fig 3. Method of suspending a painted panel.

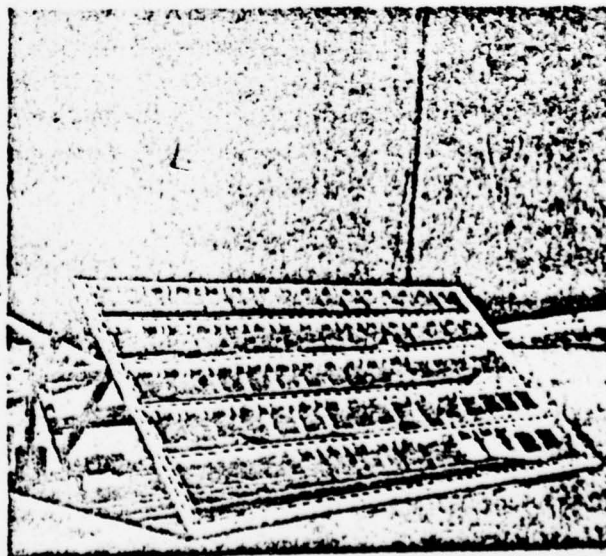


Fig 2. The painted panels supported on the testing station.

angle of 45 with the vertical and facing south.

Place of Exposure:

The station was constructed and fixed on the roof of a building facing the sea (Institute of Oceanography and Fisheries, Alexandria). This building is on the seashore (Eastern Harbour of Alexandria).

Shape and Number of Tested Panels:

15 x 15cm mild steel panels were used and hanged by short steel joints (see Fig 3). The panels were arranged in five parallel rows; each row carries 16 panels.

The testing station was constructed in August, 1976. Seventy painted steel panels were suspended and have been exposed up to now. The results are summarised in a separate paper².

Our programme will be extended to include paint exposure tests on the coasts of the Red and Mediterranean Seas; many above water testing stations will be constructed for this purpose.

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New BOCM Silcock refinery opens at Selby

A new £500,000 technical vegetable oil refinery has been officially opened at BOCM Silcock's Mill at Selby, Yorks.

The new refinery, which will process mainly linseed, soya and rape oil, replaces the company's refinery at Hull which was closed earlier this year because the lease on the site was due to expire.

Selby was chosen because it already has an oil seed crushing plant which produces crude oil for refining. It is also centrally placed in the new road transport network.

Sir Ernest Woodruffe, former chairman of Unilever — of which BOCM Silcock is part — planted a tree at the site of the new refinery on March 9 to mark the official opening.

The refined oils are used mainly in the manufacture of paints, resins and printing inks but there is a significant export trade, especially to the Middle East construction industry.

The increase in export sales achieved has been recognised by the company being granted the International Export Association's Triple Gold Award.

Building work on the refinery started early last year and was completed in December. The aim has been to automate production as fully as possible, but allowing for a wide range of viscosity oils to be produced as well as enabling oils to be processed to customer's own specifications.

A process and quality control laboratory has been incorporated to maintain high production standards.

The refining line is based upon a three centrifuge Laval separation system giving a continuous throughput on three shifts. Removal of free fatty acids and anti-oxidants is effected at this stage. The neutral oil then passes to two bleaching vessels and self-cleaning filters which are all rotated and changed over automatically, the whole operation being con-



The centrifuges and control panel at the new BOCM Silcock technical oil refinery at Selby.

trolled from a single panel. The oil storage building is designed to give speedy bulk loading and drum filling.

Oil oxidation is still based upon a batch system as this does not lend itself easily to automation and is highly dependent upon human expertise.

GEL PERMEATION CHROMATOGRAPHY (from page 10)

ments were made for air, water and formaldehyde (composite peak), phenol, mono- and dimethylphenols.

These authors also discuss the use of nuclear magnetic resonance spectroscopy combined with magnesium dioxide oxidation procedure, which differentiates between methylol and methylene eth protons, to determine the chemical structure of a bulk resin which was found to be dependent upon the formaldehyde-phenol ratio and the catalyst employed. These procedures could obviously be used to examine the individual fractions that were evident in the GPC traces.

To be continued in the May issue.

DOCUMENT

(7)

Classification of Some Commercial Inhibitive
Pigments.

Paint Manufacture, 36, January-February 1978

By

M.A. Abou-Ehalil

Classification of Some Commercial Inhibitive Pigments

by

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Pigments, National Research
Centre, Dokki, Cairo, Egypt.

It has been suggested^{1, 2}, that there are at least two ways in which a pigment may yield soluble inhibitive materials: 1—The pigment may be an inhibitive of limited solubility; 2—The pigment may be basic and so forms soaps when ground in linseed oil (in the presence of water and oxygen the soaps autoxidise to form soluble inhibitive degradation products).

The aim of the present work is to classify some new commercial inhibitive pigments according to the way by which they give inhibitive materials.

Materials and methods

Materials

Inhibitive Pigments

- 1—Zinc salt of an organic nitrogen compound (Sicorin RZ): Obtained from Hardy and Company, England.
- 2—Calcium phosphosilicate (Halox CW-111): Obtained from Halox Pigments, England.
- 3—Calcium borosilicate (Halox CW-221): Supplied by the previous company.
- 4—Basic zinc molybdate (Molywhite 101): Obtained from Sherwin Williams Chemicals, England.
- 5—Zinc phosphate: Obtained from Imperial Smelting Corporation, England.
- 6—Barium metaborate (Baran 11 M1): Obtained from Buckman Laboratories, USA.
- 7—Basic lead silicochromate (Oncor M50): Supplied by National Lead Company, USA.
- 8—Basic zinc chromate: Obtained from ICI Ltd, England.
- 9—Red Lead: Obtained from Associated Lead Manufacturers Ltd, England.

Varnish

Linseed Oil and Stand Oil Mixture: Prepared in the weight ratio of 3:2. The stand oil was added to improve the flow and water resistance properties of the linseed oil. Naphthenate driers were added until the varnish contained 0.05% cobalt, 0.08% calcium and 0.02% manganese.

Seven new commercial inhibitive pigments were tested and could be classified, according to the manner by which they yield inhibitive material, into two groups. The tests included immersion of mild steel specimens in aqueous extracts from the pigments or their paints.

Methods

1 Steel preparation³:

Mild steel specimens 50mm by 20mm were used. The specimens were washed in xylene and acetone, before immersion for fifteen seconds in concentrated hydrochloric acid. After a brief wash in distilled water, they were washed twice in methanol and twice in acetone. Specimens were dried on filter paper in an air-stream and stored in a glass-free desiccator, over silica gel, for three days before use.

2 Immersion in aqueous extracts from pigments⁴:

A few grams of each pigment were placed in small glass beakers and 50ml of distilled water were added. The beakers were kept at 25°C, under a bell-jar with a water seal and stirred occasionally for two weeks. The previously prepared mild steel specimens were then partially immersed in the pigment extracts (see fig 1). The test was carried out in quadruplicate and at the end of the test (28 days) the condition of each specimen was recorded.

3 Immersion in aqueous extracts from paints⁴:

The pigments, which have not given inhibitive aqueous extracts, were dispersed into a linseed oil-stand oil mixture, described before in the materials. Forty per cent by weight of each pigment was ball-milled with the

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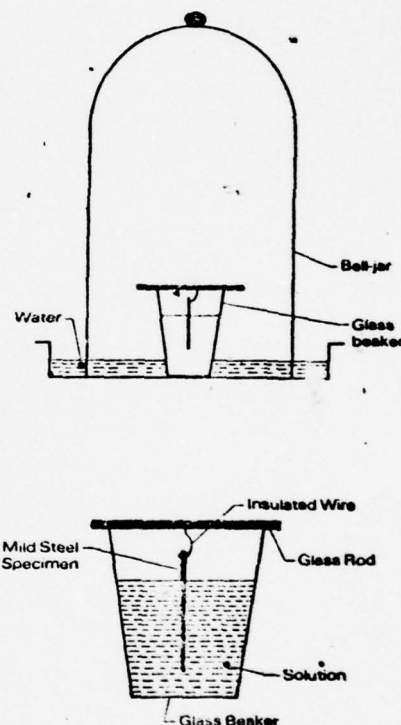


Fig 1. Immersion test equipment.

drying oil mixture and the resulting paints were applied to the interior of small glass beakers. The paints were allowed to dry for three days before 50ml of water were added. The beakers were allowed to stand two weeks at 25°C, under a water seal (see fig 1), after which time, pickled mild steel specimens were partially immersed for 28 days and the condition of each specimen was recorded.

Experimental results and discussions

The immersion of mild steel specimens in aqueous extracts from the tested pigments gave the results summarised in Table 1. A typical soluble inhibitive pigment, basic zinc chromate was used as a reference.

It was found that only two of the pigments yielded soluble inhibitive

extracts. These pigments are: 1- Organic zinc salt (Sicorin RZ) and 1- Basic lead silicochromate (Oncor M50), thus these pigments could be considered as soluble inhibitive pigments while the other pigments should be further tested.

The condition of each mild steel specimen, after immersion in extracts from paints based on the tested pigments, is described in Table 2. Basic lead silicochromate pigment was included in this test, owing to its lead composition.

From Table 2, it is clear that calcium phosphosilicate, calcium borosilicate, basic zinc molybdate, barium metaborate and basic lead silicochromate interact with drying oil mixture to produce inhibitive materials. Basic lead silicochromate seems to yield inhibitive material soluble in water and at the same time reacts with the drying oil mixture to produce soluble aqueous inhibitive extracts. This double behaviour may be attributed to the presence of chromium (limited water soluble) and lead (basic) in its composition. Zinc phosphate pigment did not give inhibitive materials either as a pigment or paint. In spite of many researches having been carried out on basic lead silicochromate³ and zinc phosphate⁷, these pigments seem to need more study.

Conclusions

The following conclusions have been drawn:

- 1 Zinc salt of an organic nitrogen compound (Sicorin RZ) is a soluble inhibitive pigment.

Table 1. Aqueous extracts from the commercial inhibitive pigments

Pigment	Specimen Condition†	Classification
Basic zinc chromate*	0	Inhibitive
Zinc salt of an organic compound (Sicorin RZ)	0	Inhibitive
Calcium phosphosilicate (Halox CW-111)	2	Non-inhibitive
Calcium borosilicate (Halox CW-221)	1	Borderline
Basic zinc molybdate (Molywhite 101)	1	Borderline
Zinc phosphate	1	Borderline
Barium metaborate (Busan 11-M1)	2	Non-inhibitive
Basic lead silicochromate (Oncor M50)	0	Inhibitive

*Used as a reference

†0 = None rusted; 1 = Light rusted; 2 = Heavy rusted.

Table 2. Aqueous extracts from pigmented drying oil paints

Pigment	Specimen condition	Classification
Red lead*	0	Inhibitive
Calcium phosphosilicate (Halox CW-111)	0	Inhibitive
Calcium borosilicate (Halox CW-221)	0	Inhibitive
Basic zinc molybdate (Molywhite 101)	0	Inhibitive
Zinc phosphate	1	Non-inhibitive
Barium metaborate (Busan 11-M1)	0	Inhibitive
Basic lead silicochromate (Oncor M50)	0	Inhibitive

*Used as a reference

2 Calcium phosphosilicate (Halox CW-111), calcium borosilicate (Halox CW-221), basic zinc molybdate (Molywhite 101) and barium metaborate (Busan 11-M1) pigments are drying oil derived inhibitors.

3 Basic lead silicochromate (Oncor M50) and zinc phosphate pigments need more study.

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DOCUMENT

(8)

Anti-Corrosion Behaviour of Some Laboratory

Prepared Barium Metaborate Based Paints.

Pigment and Resin Technology, 6, March 1978.

By

S.M. El-Saawy, M.A. Abou-Khalil and N.A. Ghanem

Anti-corrosion behaviour of some laboratory prepared barium metaborate based paints

By S. M. El-Saawy, MA, Abou-Khalil* and
N. A. Ghanem

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Research Centre, Dokki, Cairo, Egypt

Summary

Seventy paints were prepared, based on six grades of laboratory prepared barium metaborate pigments. The paints could be classified into three groups according to the type of the binder; each group comprises seven sub-groups. The paints were tested first in the laboratory and then in actual environment (above and under sea water). Commercial barium metaborate (Busan 11-M1) based-paints were prepared and used as a blank *reference*.

The laboratory prepared barium metaborate pigment-based paints showed anticorrosion behaviour similar to the commercial barium metaborate-based paints. It seemed that the paints based on barium metaborate pigment, as an inhibitive pigment, are suitable only for above water purposes.

Introduction

The present investigation describes developments in barium metaborate-based paints studies in a research work entitled "Preparation, Modification and Evaluation of some New Anticorrosive Pigments" which includes the following:

1. Laboratory preparation, modification and evaluation of barium metaborate pigments.
2. Incorporating the prepared barium metaborate pigments into formulations and testing them in the laboratory and in actual environment.

Six grades of barium metaborate pigments were laboratory prepared, modified and evaluated as pigments; the results are summarised in a separate paper⁽¹⁾. The prepared pigments were then incorporated, with other ingredients, into formula-

tions. The testing of these formulations is the main subject of the present work.

Seventy formulations based on the six prepared barium metaborate pigments, were prepared using three different types of binder. The ultimate aim of this work is to evaluate the formulation based on the prepared barium metaborate pigment by testing them first in the laboratory, using standard methods, and then in actual environment.

Materials and methods

1. Materials

1. Laboratory prepared barium metaborate pigments:⁽¹⁾

Six grades of pigments were laboratory prepared, their compositions are given in Table 1.

Pigment	Barium metaborate %	Silica %
NBM	100	—
BM-5	95	5
BM-10	90	10
BM-15	85	15
BM-20	80	20
BM-20Q	80	20 (quartz)

2. Commercial barium metaborate pigment (Busan 11-M1):

Was obtained from Buckman Laboratories, USA.

3. Red iron oxide:

Obtained from Bayer, Leverkusen, Germany

4. Red iron oxide (130F7):

Supplied by Bayer, Germany.

*Cambridge University, Department of Metallurgy
and Materials Science, Cambridge.

5. Barytes:

Was obtained from the General Company for Trading and Chemicals, Cairo, Egypt.

6. China clay:

Obtained from English China Clays Company, Ltd, England.

7. Vinyl copolymer resin (Larollex MP35):

Was obtained from BASF, Ludwigshafen, Germany.

8. Coumarone-indene resin:

Supplied by R. H. Cole Ltd, England.

9. Phenolic resin (Wresinyl 265 (R552)):

Was obtained from Resinous Chemicals Ltd, England.

10. Rosin-modified phenolic resin (Wresinate 1 (R201)):

Obtained from Resinous Chemicals Ltd, England.

11. Plasticizers (chlorinated paraffin N50):

Supplied by BASF, Germany.

12. Synthetic sea water:

Was laboratory prepared according to Warmwell.⁽²⁾

2. Methods**1. Laboratory preparation of barium metaborate Pigments.⁽¹⁾**

Is described in a separate paper.

2. Preparation of the paint:⁽³⁾

The pigment mixture was ball-milled with some of vehicle solution, for four hours. The remainder of the vehicle was then added to get the ready mixed paint.

3. Preparation of mild steel plates:⁽⁴⁾

The method was described in a previous paper.¹

4. Acid resistance test:⁽⁵⁾

Glass plates painted with the tested paints were partially immersed in 20% hydrochloric acid solution for 168 hours at room temperature. The plates were then removed, washed with water and dried. The condition of each plate was recorded.

5. Alkali resistance test:⁽⁶⁾

Painted glass plates were partially immersed in 5% sodium hydroxide solution and left for 168 hours. The plates were then removed, washed and dried, and the condition of each plate was then recorded.

6. Hardness measurements:⁽⁶⁾

The Albert König rocker tester was employed for comparison of hardness of the tested paints.

7. Laboratory corrosion resistance test:⁽⁷⁾

Mild steel specimens, 5 x 10cm, were painted and allowed to dry and then edged with wax. They were scratched to expose the bare metal and then immersed in synthetic sea water for up to 670 hours. The condition of each specimen was recorded.

8. Environmental exposure test:

a. Above water: The test includes the exposure of mild steel plates, 15 x 15cm, to the actual conditions. The plates were covered by three coats of the tested paint and allowed to dry and then supported to a testing station. A description for this station is given in a separate paper. The exposure was carried out in Alexandria and has been continued up to now (more than one year).

b. Underwater: The mild steel plates were painted first by three coats of the tested paint followed by one of antifouling composition. The plates were then supported to a painted steel stands (see Fig 1). The test was carried out in a specially built floating station in the Eastern-harbour water of Alexandria. (A description of this station will be given in the April issue of *Pigment & Resin Technology*).

Experimental results and discussions

Seventy paints based on barium metaborate pigment, were laboratory prepared and could be classified into three groups. Each group of paints comprises seven sub-groups. The compositions of the prepared paints are summarized in Tables 2, 3 and 4.

Commercial barium metaborate (Busan 11-**Table 2. Paint Film Compositions of Paints Group No. 1**

	Sub-group 1				Sub-group 2				Sub-group 3				Sub-group 4				Sub-group 5				Sub-group 6				Sub-group 7			
Composition	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
CBM*	20	30	40	50																								
NBM					20	30	40	50																				
BM-5									20	30	40	50																
BM-10													20	30	40	50												
BM-15																	20	30	40	50								
BM-20																					20	30	40	50				
BM-20Q																									20	30	40	50
Red iron oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
Barytes	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—
China clay	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
Vinyl copolymer	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	27	
Plasticizers	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
Coumarone-indene	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	
Total pigment	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	
Total binder	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	
Pigment: binder	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	

* Commercial barium metaborate (Busan 11-M1)

M1) was used as a blank and formulations, based on it, were prepared and put in separate sub-groups. All the formulations contained red iron oxide, barytes and china clay as inert pigments.

Paints Group No I

This group of paints comprises twenty eight formulations, based mainly on a neutral binder (a mixture of vinyl copolymer and coumarone-indene resin (3:1)). According to the type of the inhibitive pigment, this group could be classified into seven sub-groups and each sub-group comprises four formulations. The percentage of the inhibitive pigment ranges from 20 to 50% of the total paint film.

All the tested paints of this group passed both acid and alkali resistance tests without failure. They also passed the laboratory corrosion scratch test which continued for up to 670 hours and the rust was formed only in the grooves without spreading.

The atmospheric exposure of these paints was carried out in Alexandria close to the sea-shore, on an exposure testing station and continued for more than one year. The inspection of these paints, at the end of the test, has showed no rust formation and also no change in colour. It seems that this group of paints could resist the severe atmospheric conditions for up to one year.

Mild steel painted plates were immersed in sea water, after being coated by a layer of anti-fouling composition. The inspection was carried out monthly and photographs were taken (see Figs 1 and 2).

The paints, based on laboratory prepared barium metaborate pigments, have shown blistering at the end of three months immersion. The commercial barium metaborate-based paints showed blistering within eight months immersion. The blistering was formed without accompanying rust or damage. These paints seem to be unsuitable for underwater purposes.

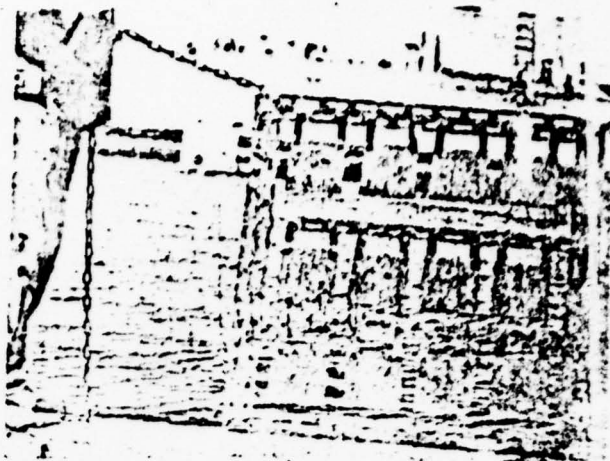


Fig 1. The painted plates before underwater immersion.

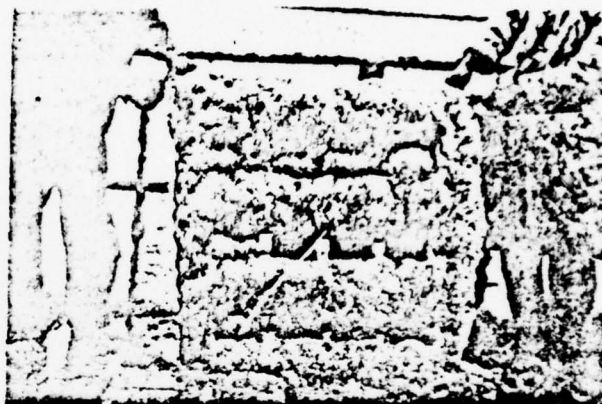


Fig 2. The painted plates after four months immersion in sea water.

Paints Group No II

The aim of preparing the paints of this group is to study the effect of replacing a part of the neutral binder, used in paints group No I, by phenolic and rosin-phenolic resins (acidic resin). Twenty eight formulations were prepared based on a mix-

Table 3. Paint Film Compositions of Paints Group No. II

	Sub-group 1				Sub-group 2				Sub-group 3				Sub-group 4				Sub-group 5				Sub-group 6				Sub-group 7			
Composition	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56
CBM*	20	30	40	50	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NBM	—	—	—	—	20	30	40	50	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
BM-5	—	—	—	—	—	—	—	—	20	30	40	50	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
BM-10	—	—	—	—	—	—	—	—	—	—	—	—	20	30	40	50	—	—	—	—	—	—	—	—	—	—	—	—
BM-15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	20	30	40	50	—	—	—	—	—	—	—	—
BM-20	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	20	30	40	50	—	—	—	—
FM-20Q	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	20	30	40	50
Red iron oxide	—	—	—	—	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Barytes	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—	30	20	10	—
China clay	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Vinyl copolymer	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
Plasticizers	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Phenolic resin	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Rosin-phenolic resin	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Total pigment	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Total binder	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40
Pigment: binder	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

*Commercial barium metaborate (Busan 11-M1)

Table 4. Paint Film Compositions of Paints Group No. III

Composition	Sub-group 1		Sub-group 2		Sub-group 3		Sub-group 4		Sub-group 5		Sub-group 6		Sub-group 7	
	57	58	59	60	61	62	63	64	65	66	67	68	69	70
CBM*	30	50	—	—	—	—	—	—	—	—	—	—	—	—
NUM	—	—	30	50	—	—	—	—	—	—	—	—	—	—
BM-5	—	—	—	—	30	50	—	—	—	—	—	—	—	—
BM-10	—	—	—	—	—	—	30	50	—	—	—	—	—	—
BM-15	—	—	—	—	—	—	—	—	30	50	—	—	—	—
BM-20	—	—	—	—	—	—	—	—	—	—	30	50	—	—
BM-20Q	—	—	—	—	—	—	—	—	—	—	—	—	30	50
Red iron oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Barytes	20	—	20	—	20	—	20	—	20	—	20	—	20	—
China clay	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Phenolic resin	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Rosin-phenolic	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Total pigment	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Total binder	40	40	40	40	40	40	40	40	40	40	40	40	40	40
Pigment: binder	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

*Commercial barium metaborate (Busan 11-M1).

ture of vinyl copolymer, phenolic and rosin-phenolic resin (acidic) (2:1:1).

The laboratory and exposure tests of these paints have shown similar behaviours as paints of group No I.

Paints Group No III

In this group of paints a mixture of phenolic and rosin-phenolic resin (3:1) was used as a main binder and fourteen formulations based on it prepared and classified into two sub-groups.

This group of paints passed both the acid and alkali tests to some extent. Most of the paints films of this group were broken down on laboratory corrosion testing with the formation of rust between the films and the substrates. This behaviour may be due to the type of the binder used.

The atmospheric and immersion exposure tests for these paints gave the same results as paints groups No I and II.

The paint films of all groups were removed from the substrates, at the end of immersion tests (3 months); the conditions of the mild steel plates were then recorded. The substrates were found clean with no rust. The solutions formed between the substrates and the paint films (blistering), were found alkaline in nature (pH 10.5). This explains why the mild steel substrates did not show rust, in spite of being shown blistering. This high pH may

be attributed to the solubility of the barium metaborate (0.3g/100mls H₂O) which makes the water, in intimate contact to the substrates, alkaline and thus discourages rust formation.

Conclusions

The following conclusions have been drawn:

1. The paints based on the laboratory prepared six grades of barium metaborate showed good corrosion resistance against severe conditions.
2. All the prepared barium metaborate-based paints showed the same anti-corrosion behaviour, irrespective of silica content.
3. The formulations based on vinyl copolymer and coumarone-indene resin (3:1) or vinyl copolymer and phenolic resins (1:1) were more effective against corrosion than those based on phenolic resins only.
4. The barium metaborate-based paints seem to be more suitable for above water purposes.

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